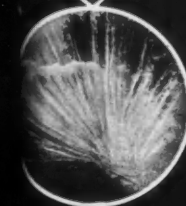


CHEMISTRY



✓

Experimenting With Chemistry

SEP 30 1957

DURHAM, N. C.

By BURTON L. HAWK

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Editorial:

Before You Experiment
Inside Front Cover

\$1.00

Before You Experiment

► "EXPERIMENTING WITH CHEMISTRY" is designed primarily for the home "do-it-yourself" chemist. It is assumed the experimenter has graduated from the chemistry set, has enlarged his laboratory, and now is ready for more advanced and varied fare.

Experimenting with chemistry at home has gained an undeserved reputation as a dangerous pastime. This is not true if ordinary common sense is exercised. If you place your fingers into a live electric socket, you will experience severe shock. Or, if you insist on inhaling illuminating gas from the kitchen stove, you will succeed in asphyxiating yourself. Thus, we could say that electricity and gas are too dangerous to have in the home.

Certainly electricity and gas are dangerous if not treated with respect. But using basic knowledge and common sense, we can use these commodities in complete safety and to great advantage. So it is with experimenting. If you work carefully, using common sense and heeding warnings, experiments can be performed with complete safety.

You need not be afraid to perform any of the experiments in this book, *IF* you heed the warnings and abide by the instructions given. And remember these general rules that apply to all of the experiments:

1. *Keep your face away from boiling or reacting compounds.*
2. *Use only small quantities.*
3. *Provide adequate ventilation.*
4. *Keep chemicals away from skin and clothing.*

This is not a text, but is intended solely for your pleasure in pursuing the fascinating science of chemistry. It is our hope that you will find sufficient inspiration here to delve deeper into the subject and perhaps find in it the real satisfaction of contributing your talents to full-time research for the advancement of science.

BURTON L. HAWK

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Chapter I

Experimenting With Gases

► THE AIR WE BREATHE is so commonplace we give it but little thought. Yet the gases that compose this air have quite remarkable properties in themselves. We shall prepare three gases of the air in their pure form: *oxygen*, *carbon dioxide*, and *nitrogen*, and then will examine some of their individual properties. We shall consider two of these gases — nitrogen

and oxygen—in combined form. You will find that the compounds thus obtained are quite different from the oxygen and nitrogen alone! We will then investigate the popular *ammonia*, followed by quite a different character — the poisonous but highly useful element — *chlorine*. Finally, we will examine the versatile properties of *sulfur dioxide*.

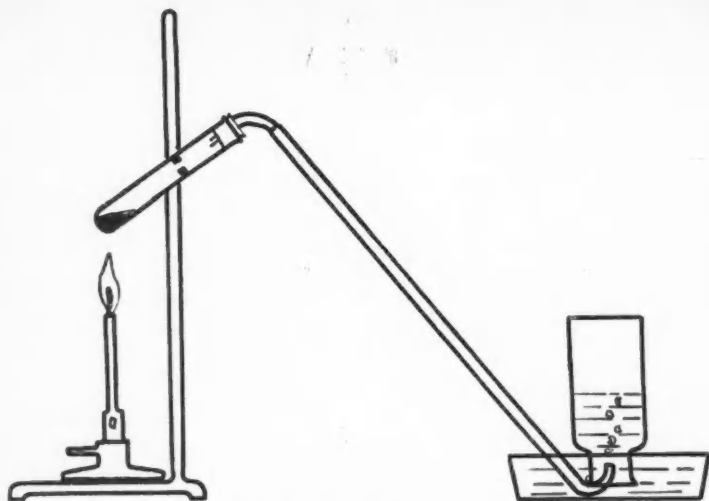
1. Oxygen

► ALTHOUGH OXYGEN comprises only 21% of the air, it is by far the most active component. Of course, it is essential to life. It combines with most other substances at elevated temperatures, accompanied by flame. We call this procedure "combustion" and oxygen a "supporter of combustion." Naturally, if a substance burns readily in air, you can imagine how much more rapidly it will burn in pure oxygen. This can be demonstrated in the home laboratory in an exciting display of pyrotechnics.

It is rather difficult to obtain oxygen in a pure state from the atmosphere. Thus we will obtain it from compounds. Potassium chlorate, for instance, contains oxygen which is readily released by heating: $2\text{KClO}_3 \rightarrow 2\text{KCl} + 3\text{O}_2$. If we should add manganese dioxide, the oxygen is liberated at a much lower temperature. The manganese dioxide, merely acts as a *catalyst* in this reaction and remains unchanged. In some manner, not clearly understood, it forces the potassium chlorate to release its oxygen faster.

Mix together thoroughly and carefully 5 grams of potassium chlorate with 2 grams of manganese dioxide. Mix the chemicals on a clean piece of paper with a spatula. Do not grind or crush! Transfer the mixture into a large dry test tube. Heat the tube gently and evenly. The gas is collected over water as shown in the accompanying diagram. The test tube is fitted with a one-hole stopper and glass tubing. Rubber tubing is fitted to the glass tubing and extends to the jar of water inverted in a trough of water. As the oxygen is liberated, it bubbles through the water and pushes it out of the jar. Cover the jar with a wet glass plate and set it upright on the table. Collect as many bottles of oxygen as you can in this manner. When you are through, be sure to disconnect the rubber tubing before you remove the flame. This will prevent the water from being sucked back into the hot test tube.

Obtain a splinter of wood. Ignite it, then extinguish the flame until only a spark is still glowing. Immerse the glowing splinter into a bottle of



➤ *Preparation of oxygen.*

oxygen. It will burst into flame and will continue to burn vigorously.

Ignite a tuft of steel wool by holding it in the alcohol lamp flame for a minute. Immerse the glowing wire into a bottle of oxygen. You will enjoy the sparkling display.

Charcoal will burn brilliantly in oxygen. Insert a glowing piece into a bottle and observe for yourself.

There are many other items that you can burn in oxygen with spectacular results. Magnesium metal burns with a blinding white light.

Sulfur burns with a large blue flame. Phosphorus burns with a bright yellow flame evolving large clouds of dense white smoke. In fact, any combustible substance will burn rapidly in pure oxygen.

You can devise other tricks and experiments with oxygen. Try placing moist iron filings in a bottle and note how quickly they rust. Or you can place a fly or beetle in oxygen and see how it reacts. You can even take a sniff yourself and see how you react!

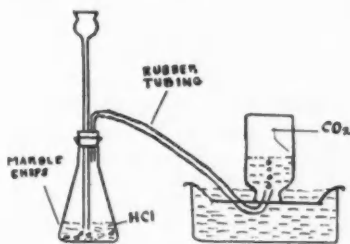
2. Carbon Dioxide

➤ CARBON DIOXIDE is an amiable substance to use. It is not poisonous, does not explode, and has no odor; therefore it will not be necessary to drive the rest of the family out of the house while we are experimenting.

The formation of carbon dioxide is very easy. Simply exhale. That this CO_2 is as good as any other CO_2 can be proven by blowing through a glass tube into a solution of lime water. A white precipitate of calcium

carbonate will form. Or blow through a weak solution of sodium carbonate colored pink with phenolphthalein. It will turn white. Or better still, blow into a blue solution of litmus and it will turn red. Here is an opportunity for you to show your friends how strong your breath is. But this method of obtaining carbon dioxide will become exhausting, so let us proceed from here by chemical means.

Place a few teaspoonfuls of marble chips (technically, calcium carbonate) in a large flask and cover with water. Fit the flask with a stopper containing a delivery tube and thistle tube. Since carbon dioxide is heavier than air, you may prepare it by downward displacement of air. Or, if you prefer, it can be collected over water. Pour hydrochloric acid through the thistle tube and collect several bottles of the gas. It may be necessary to add more acid from time to time to insure an even flow of gas.



Did you know that carbon dioxide supports combustion? Neither did we, because it doesn't. But some active metals will continue to burn in it. To demonstrate, ignite a piece of magnesium ribbon and thrust it into a bottle of carbon dioxide. It will continue to burn and soot will be formed.

If you have ever had a chemistry set, you are probably familiar with the stunt of pouring carbon dioxide over a lighted candle. The flame will be extinguished, seemingly by holding an 'empty' bottle over it.

Place a dry container of CO_2 on the table. Remove the lid just before you are ready to perform the experiment. Now prepare a solution of blue litmus. Pour the blue solution into the jar of CO_2 and shake. It will mysteriously turn red. This is most baffling to one not familiar with the deep complications of chemistry. Let your unsuspecting friend try the trick. Direct him to pour the blue solution into an empty bottle. He can shake all day, but it won't turn red. Next you pour the solution into another bottle (note: your bottle contains CO_2) and the color changes.

The next trick requires much patience. First it is necessary to fill a small shallow pan completely with carbon dioxide. Connect a rubber hose to your generator leading to the bottom of the pan. Allow gas to flow into the pan for quite some time. Now, while gas is still flowing in, blow a few soap bubbles and direct them so that they float easily down into the pan. If sufficient gas is in the pan, the bubbles will float on top of it, dancing mysteriously in mid air.

Solid CO_2

Carbon dioxide is very easily liquified. If this liquid, under pressure, is allowed to escape into a cloth bag, the evaporation and expansion cause absorption of heat and part of the liquid solidifies. This solid CO_2 is widely used as a refrigerant under the name of *Dry Ice*.

You can prove that dry ice is car-

bon dioxide by placing a piece in a dry flask. Attach a delivery tube leading into lime water. As the solid sublimes, the CO_2 will bubble through the lime water and turn it milky.

Place a solid stopper in the flask—not too tightly—and see how long it

will take the expanding gas to blow it out.

The same stunts described for CO_2 gas can also be performed using solid CO_2 . However, do not pick up the ice with your bare hands; always use gloves or tongs.

3. Nitrogen

► IT MAY SURPRISE the average man to know that the greatest part of the air he breathes is not oxygen — but nitrogen. We have grown so familiar with the oxygen-carbon dioxide cycle, that we are prone to forget nitrogen which actually comprises 78% of the atmosphere.

We think of nitrogen in the air as a “useless” substance simply because it is inert. Actually, it is extremely important. Its presence dilutes the oxygen and thus slows down the process of oxidation. Without it, burning would be too rapid — decay and rust would run rampant—life would probably be much shorter.

Then there is the nitrogen cycle to consider. A special type of “nitrogen-fixing” bacteria which is present under the roots of leguminous plants (clover, peas, alfalfa, etc.) converts the free nitrogen of the air into nitrogen compounds which the plants can use. Finally, when living things die, decomposition sets in and eventually free nitrogen is restored again to the atmosphere. Thus the cycle repeats itself again and again, as it has since the dim beginnings of life and probably will until the end of time. By this remarkable process of fixation and decomposition the ratio of nitrogen to oxygen remains constant.

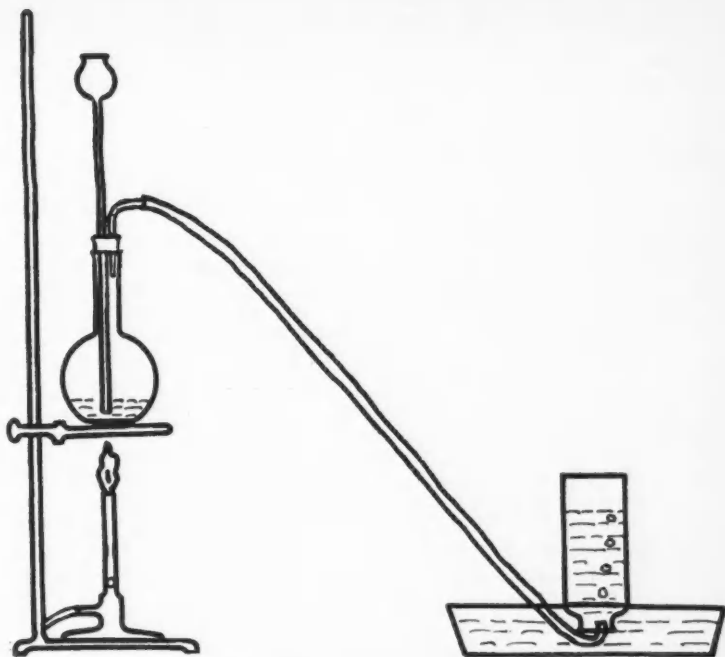
Nitrogen can be obtained from the atmosphere, but it is a rather difficult and cumbersome process for the home laboratory. Commercially, the air is liquefied and the nitrogen separated by fractional distillation.

In the laboratory, nitrogen can be obtained conveniently from its compounds. Ammonium nitrite, when heated, decomposes into pure nitrogen and water:



However, since ammonium nitrite is very unstable, there is some danger of explosion when it is heated. To avoid this danger, the ammonium nitrite is simultaneously prepared and decomposed in aqueous solution.

Mix together 5 grams of sodium nitrite with 4 grams of ammonium chloride in a large flask. Set up an apparatus designed to collect the gas over water, as shown in the accompanying diagram. Add about 30 cc. of water through the thistle tube and heat the flask gently. Allow the gas to bubble through the water in the trough a short time before collecting. When the bubbles form rapidly, place the rubber tube under the bottles in the trough and remove the flame from the flask. The nitrogen will displace the water in the inverted bottles. If



➤ COLLECTING *nitrogen* over water.

the action in the flask should become too violent, pour in more cold water. If the bubbles form too slowly, apply heat again *gently*. Collect several bottles of the gas. Cover with a glass plate and remove the bottles from the trough.

Now that you have gone to all the trouble of preparing nitrogen, about the only thing you can do with it is throw it away. As we pointed out before, nitrogen gas is reluctant to combine with other elements at ordinary temperatures. It, of course, does not support ordinary combustion. Insert a burning splinter of wood into a jar

of nitrogen. It will be extinguished immediately.

However, magnesium will continue to burn in nitrogen to form the *nitride*, Mg_3N_2 . Ignite a small strip of the metal and insert in a jar of nitrogen.

Carefully remove the white residue, grind to a powder and add a few drops of water. Do you recognize the odor of ammonia?

That's about all we can do with nitrogen in the laboratory. Nothing spectacular about it,—but a mighty important element!

4. Oxides of Nitrogen

► TO GIVE EXPRESSION to the private opinion of most chemistry students, the chief objection to the oxides of nitrogen is that there are too many of them. It is rather interesting to note that oxygen and nitrogen, which exist together in the elemental state under all atmospheric conditions, are capable of uniting with each other to form five different compounds. These compounds have somewhat unusual properties, and it will be worth our while to consider them in detail.

Nitrous Oxide, N_2O

► BETTER KNOWN as "laughing gas" or "sweet air," nitrous oxide has been used as an anesthetic — it is the "gas" the dentist used during extraction of teeth, although today it is being replaced with local anesthetics such as novocaine and related compounds. When inhaled it produces somewhat intoxicating effects similar to those produced by an over-indulgence in alcoholic beverages — so we have been told.

In order to study the properties of the gas, set up an apparatus whereby you can collect several bottles of it over water — preferably warm water — similar to the method used to collect oxygen. Use a flask as your generator fitted with a two-hole stopper, thistle tube, and delivery tube. Cover the bottom of the flask with pieces of mossy zinc. Pour 10 cc. of con. nitric acid in 100 cc. of water and transfer the mixture to the flask. If the reaction is too slow, heat until a steady stream of gas is given off and you are able to collect several bottles of it.

One striking property of nitrous

oxide is its ability to support combustion. Glowing splinters, steel wool, sulfur, etc. burn almost as brightly in nitrous oxide as in oxygen. You can demonstrate this property readily in the home laboratory.

Nitrous oxide can also be obtained by heating ammonium nitrate; however, this method is rather dangerous and we do not recommend it for the home chemist. Being of a temperamental nature, ammonium nitrate is not to be trusted. If heated too strongly or unevenly, it may explode violently.

In 1921 a terrific explosion completely demolished a chemical plant in Germany devoted to the manufacture of ammonium nitrate. The factory disappeared entirely, leaving an enormous crater in the earth over fifty feet deep — grim evidence of the explosive potentiality of this compound! The Texas City disaster in 1947 was also due to an ammonium nitrate explosion.

Nitric Oxide, NO

► PLACE A FRESH quantity of zinc in your generator flask, and this time add to it a mixture of 5 cc. con. nitric acid and 20 cc. of water. The action will be more vigorous than before, and the flask will become filled with brown fumes. Wait until the brown fumes disappear, then collect a bottle or two of the gas, as before. Nitric oxide is colorless, but it readily reacts with oxygen to form the brown nitrogen dioxide, which explains why the brown fumes were observed at first

in the flask. Remove the cover from one of your bottles of colorless nitric oxide; it will turn brown. Here is an opportunity for you to create a few "magic" experiments to fool your friends. You can show them a bottle of colorless "air" which will be colored brown merely by removing the stopper — or by blowing in the bottle, etc.

One important reaction of nitric oxide is with ferrous sulfate. Allow the gas to bubble through a solution of ferrous sulfate for a few minutes and notice the color change. This reaction is the basis of the familiar "brown-ring" test for nitrates. The nitrate solution is mixed with ferrous sulfate solution and con. sulfuric acid is added. The sulfuric acid liberates nitric acid from the nitrate, and this in turn is reduced to nitric oxide:

$6\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 + 2\text{HNO}_3 \rightarrow 3\text{Fe}_2(\text{SO}_4)_3 + 2\text{NO} + 4\text{H}_2\text{O}$. The nitric oxide then forms the brown compound with ferrous sulfate ($\text{FeNO} \cdot \text{SO}_4$) which identifies the nitrate.

Nitrogen Dioxide, NO_2 , or Dinitrogen Tetroxide, N_2O_4

➤ WE HAVE ALREADY prepared nitrogen dioxide by allowing nitric oxide to react with air. To prepare in quantity, add 5 cc. of con. nitric acid to zinc in a large flask. The action is quite vigorous and large clouds of red-brown gas are given off. (Caution—poisonous! Do not inhale!). Invert an empty flask above the generator to catch the gas. When filled with the brown fumes, stopper it.

Nitrogen dioxide is unique in that it changes color with the temperature.

At low temperatures it is a yellow liquid; as the temperature rises it changes to a colorless gas, then pale yellow, light brown, and finally dark red-brown. The yellow liquid has the formula N_2O_4 and is a *polymer* of NO_2 . At normal temperatures, both forms exist as a mixture.

You can observe the color changes of the gas by immersing the flask containing it in cold water. As the temperature drops, note the lighter color. By immersing the flask in warm water, the color darkens.

Nitrogen Trioxide, N_2O_3

➤ THE TRIOXIDE is the least familiar member of the family. It is obtained by evaporating a mixture of nitrogen dioxide and ozone. It is soluble in water but does not combine with it.

Nitrogen trioxide is formed temporarily when sulfuric acid is added to a nitrite, but under normal conditions decomposes rapidly into a mixture of NO_2 and NO . Prepare a solution of sodium nitrite and add to it a small quantity of dilute sulfuric acid. Note the deep brown fumes of nitrogen dioxide.

Nitrogen Pentoxide, N_2O_5

➤ THE ANHYDRIDE of nitric acid, N_2O_5 , is a white crystalline solid. It is not important and is difficult to obtain in a pure state. It can be produced by dehydrating nitric acid with phosphorous pentoxide.

We hope these experiments have proven of value in acquainting you more intimately with the family of oxides of nitrogen — an interesting and versatile group to say the least!

5. Ammonia

➤ MANY YEARS AGO, some observant soul noticed that a gas with a sharp stifling odor was produced when the hoofs and horns of animals were heated, and that this gas would dissolve easily in water. The solution thus obtained was called "spirit of hartshorn" and can be considered the ancestor of modern ammonia water. Ammonia is produced in nature when any nitrogenous organic material decomposes in the absence of air.

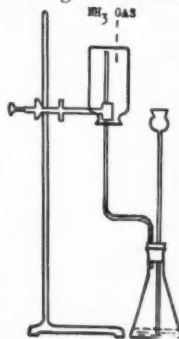
Place a few crystals of plain gelatin in a dry test tube. Apply gentle heat, trying not to scorch the material. See if you can detect the odor of ammonia at the mouth of the tube. Be sure to remove the tube from the flame before you do any sniffing. Because there are other products given off at the same time, the ammonia may be difficult to detect. Moisten a piece of red litmus paper and hold it at the mouth of the tube. It will turn blue, indicating the presence of alkali (ammonia?).

If you have a few spare fingernails that need cutting, place the trimmings in a dry test tube and add a small quantity of lime (calcium oxide or hydroxide). Heat again, as above, and test with litmus paper.

The first pure ammonia was probably prepared by Priestley, about 1774, by heating sal ammoniac with lime. Place a small quantity of ammonium chloride and an equal amount of lime in a dry test tube. Again heat and smell cautiously after removing from the flame. This time you will have no trouble in detecting the ammonia!

Before we prepare ammonia in quantity and investigate its properties, we would like to include a word of caution. Even though ammonia is used to strengthen fainting ladies and revive the unconscious, don't forget that it will also operate in the reverse. For if you inhale too strongly, it will knock you out! Remember, too, ammonia is very irritating to the eyes. Perform these experiments in well-ventilated surroundings, and keep your face a safe distance away!

The most convenient way to prepare ammonia in the laboratory is by adding ammonium hydroxide to solid potassium hydroxide. Use an Erlenmeyer flask as the generator. Place about 2 grams of potassium hydroxide pellets in the dry flask. Close the flask with a two-hole stopper containing thistle tube and glass tubing

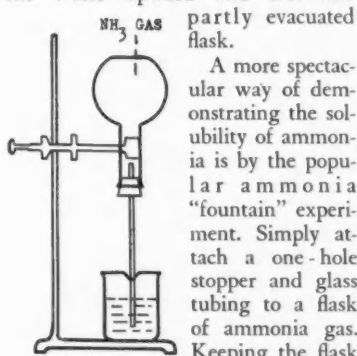


➤ FIG. 1. Collecting ammonia by downward displacement.

arranged to collect the gas by downward displacement of air (see Fig. 1). Add enough ammonium hydroxide through the thistle tube to completely cover the pellets and be sure the end of the thistle tube is entirely immersed in the liquid. The action should proceed quite vigorously by itself as pure ammonia is produced. If the reaction is slow it may be necessary to apply gentle heat. Just be careful not to heat

too strongly! Collect a few bottles of the gas, as shown in the illustration. The delivery tube should extend nearly to the bottom of the inverted receiving bottle or flask. When you estimate the flask is filled with ammonia (*estimate . . . don't smell!*) carefully remove it keeping it upside down. Ammonia is lighter than air and it will stay in the flask as long as you hold it in an inverted position. Place the flask upside down on the table.

Ammonia is very soluble in water. Take one of the flasks of ammonia and place it — still inverted — in a pan of water. After a while the water will rise up inside the flask. As the ammonia dissolves in the water, it leaves a partial vacuum in the flask. Thus atmospheric pressure then forces the water upward and into the



➤ FIG. 2. *The ammonia fountain.*

drops of phenolphthalein solution (see Fig. 2). The water will rise up the tube and when it reaches the ammonia flask will gush forth as a fountain until the flask is filled. The water will turn red, due to the phenol-

phthalein indicator added. If you like, red litmus solution may be substituted. Then you will have a blue fountain. The water rises in the tube very slowly, so be patient! If it does not rise after a reasonable length of time, then you do not have sufficient ammonia in the flask. Collect more and try again.

Ammonia is also an effective reducing agent. Place some black copper (cupric) oxide in a test tube and apply heat. Place the delivery tube from your ammonia generator about $\frac{1}{2}$ inch above the oxide in the tube. Soon you will note the black powder is turning reddish-brown as it is reduced first to cuprous oxide and then to metallic copper.

Still another example of reduction by ammonia can be shown by a sympathetic ink experiment. Write on a piece of filter paper with a solution of mercurous nitrate using a glass rod or a tooth pick. Allow to dry. The writing will be invisible. Now hold the paper near the outlet tube of the ammonia generator. The writing will suddenly appear in black characters. The ammonia has reduced the mercurous solution to metallic mercury.

Finally, take another bottle of ammonia. Turn it right side up and quickly add a few drops of hydrochloric acid and shake. Note the thick clouds of smoke forming in the flask. This "smoke" consists of tiny particles of ammonium chloride. You can create many "magic" tricks with this reaction. For example, pour a bottle of invisible hydrogen chloride gas (made by heating common salt with sulfuric acid) into a bottle of invisible ammonia gas. Thus two apparently "empty" bottles produce smoke. Or you can moisten a piece of cotton with

HCl and hold it near the mouth of a bottle of ammonia and observe smoking cotton without flame.

Of course, we do not have to elaborate on the usefulness of ammonia. It is used in huge quantities in the production of important ammonium compounds for industry and fertilizers, and is itself an important refrigerant. Further, it is oxidized to produce nitric acid which in turn is used to manufacture a host of nitrate products.

Ammonia is now produced synthetically from the nitrogen of the air and the hydrogen from water. This method was devised by the German chemist Haber during World War I to manufacture the explosives so badly needed. This is a remarkable achievement when we consider the multitude of ammonia and nitrogen compounds that can be obtained by using as the starting raw materials two abundant materials: air and water!

6. Chlorine

► LET US IMAGINE ourselves in the year 1774. And let us enter the laboratory of one Carl Wilhelm Scheele in Sweden. His laboratory is simple; he, of course has none of the modern equipment which we deem essential in our laboratories of today. He is intensely absorbed in his work. Upon closer examination we find he is experimenting with the mineral *pyrolusite*, which, he believes, contains a new substance. He now adds hydrochloric acid to a portion of pyrolusite and after a while he notices a greenish gas arising from the vessel. This commands his full attention, as he does not recall any vapor that is like this. He sniffs the gas and finds that it has a sharp suffocating odor. He is puzzled. What can this be? He is so handicapped by lack of knowledge! He does not know his acid is composed of hydrogen and chlorine. And he does not know the pyrolusite contains manganese dioxide. And he can never guess that the mineral is oxidizing the acid and thus setting the chlorine free. And, lastly, he does not realize that he has discovered a new

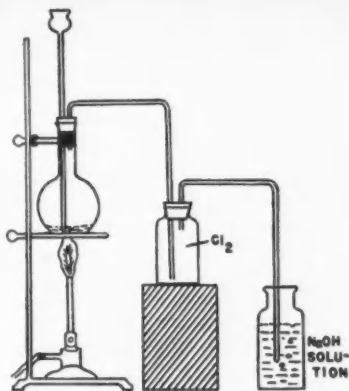
element—*chlorine*! In fact, it is considered a compound for over 36 years, when it is finally proven to be an element by none other than the illustrious Sir Humphry Davy.

Now back to the twentieth century where we can prepare the same chlorine from the same materials used by Scheele with the added advantages of purer compounds, better equipment, and more knowledge . . . we hope.

Place two or three grams—no more—of manganese dioxide in the generator flask, (see diagram). Add hydrochloric acid through the thistle tube. Apply gentle heat and collect several bottles of the gas.

The excess chlorine is allowed to bubble through a solution of sodium hydroxide where it is absorbed. Precaution must be taken, as chlorine is very poisonous. Prepare only small quantities at a time in well ventilated surroundings. Do *not* inhale the gas! If you do accidentally inhale a large quantity of chlorine, breathing ammonia fumes will relieve irritation.

Chlorine can also be obtained from



common salt. Mix equal quantities of salt and manganese dioxide (about 1 gram of each) and place in the generator. Pour dilute sulfuric acid through the thistle tube. In this reaction, hydrochloric acid is formed by the action of sulfuric acid on the salt and is immediately oxidized by the manganese dioxide.

Chlorine is extremely active as can be demonstrated by the following reactions: Powdered antimony sifted into a jar of chlorine will burst into flame forming antimony trichloride, SbCl_3 . Powdered iron, heated moderately, glows brilliantly to form ferric chloride, FeCl_3 . A piece of filter paper moistened with turpentine ignites spontaneously in chlorine, emitting large clouds of soot. Colored papers, cloths, flowers, etc., when moistened with water are bleached white by chlorine. Actually, substances are not bleached by chlorine but by the hypochlorous acid which is formed by chlorine and water. And to be still more technical, it is not the hypochlorous acid but the atomic oxygen

released by this compound that is really responsible for bleaching. Or, in a nutshell, the bleaching action of chlorine is due to oxygen . . . !

Heated copper foil will burn in the gas resulting in a mist of cupric chloride, CuCl_2 . Phosphorus burns feebly in chlorine to form the trichloride, PCl_3 , or pentachloride, PCl_5 , depending on the abundance of chlorine. (Use only a *very* small piece of phosphorus.) Melted sulfur unites to form sulfur monochloride, S_2Cl_2 . Sodium unites with chlorine to form, obviously, sodium chloride.

To prepare synthetic salt, place a small, dry, freshly-cut piece of sodium in a jar of chlorine. It might be well to place the metal in a dry deflagration spoon; then lower into the jar. Allow to stand for about 30 minutes. Close examination will then reveal a white powder which is common table salt, although a rather expensive way to prepare it. If you are skeptical, dissolve the product in a large volume of water. Use a large container in the event all sodium has not reacted. Add silver nitrate and note the white precipitate indicative of the chloride ion. We do not recommend tasting as a method of proof.

Chlorine has many uses. In peacetimes it is used in the purification of water to save lives. In war times, it is used in poison gases to destroy lives. However, its latter use is being replaced by the atom bomb, which has been found to be much more effective. It is also used in the manufacture of dyes, drugs, explosives, disinfectants, germicidal preparations, in extracting gold from its ores and in reclaiming tin from "tin" cans.

7. Sulfur Dioxide

It Is Prepared Easily

In the home lab, sulfur dioxide is most conveniently prepared by the action of dilute acids on sodium bisulfite (sodium hydrogen sulfite). In a large flask, place 2 or 3 grams of sodium bisulfite and cover the solid with about $\frac{1}{4}$ inch of water. Fit a 2-hole stopper to the flask containing a thistle tube and delivery tube. Be sure the thistle tube extends beneath the surface of the liquid in the flask. When you are ready to generate sulfur dioxide, simply pour dilute hydrochloric acid, in small quantities, through the thistle tube.

It Will Dissolve In Water

Arrange your delivery tube from the generator so that the gas will bubble through water in a test tube. It will dissolve readily forming a solution of sulfurous acid, H_2SO_3 . The acidic properties can be identified with litmus paper.

It Will De-Colorize

Bubble the gas through a dilute solution of potassium permanganate. As each bubble enters the solution, the violet color fades slightly until the solution is entirely colorless.

It Can Be Liquefied

Sulfur dioxide can be liquefied very easily at atmospheric pressure with salt and ice mixture. Insert a U-tube in a container filled with crushed ice and salt. Attach the delivery tube of your SO_2 generator to the U-tube and allow the gas to pass through. Soon you will note a colorless liquid forming in the bottom of the U-tube. This is liquid sulfur dioxide. Remove the

tube from the ice and you will observe that the liquid gradually boils away.

It Will Bleach

Fill a large jar with sulfur dioxide. Moisten a few bits of colored paper, cloth, flowers, leaves, etc. and place in the jar. Cover with a glass plate and let stand for a while. Sulfur dioxide will bleach many items (but not everything), especially silk, wool, straw and flowers, although in most cases the bleaching is not permanent.

It Will Preserve

Place half of a freshly cut red apple in a jar of sulfur dioxide. Take notice that the brown discoloration that usually takes place in air does not occur in an atmosphere of sulfur dioxide, although the red skin will be bleached. Sulfur dioxide has been used as a preservative in many foods; however, its use in this category has been questioned and is still open to argument.

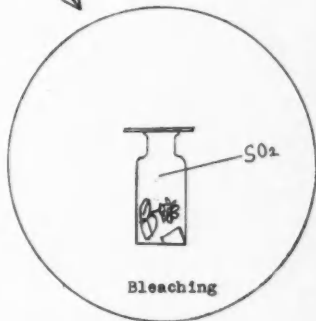
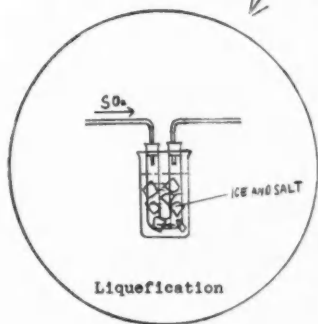
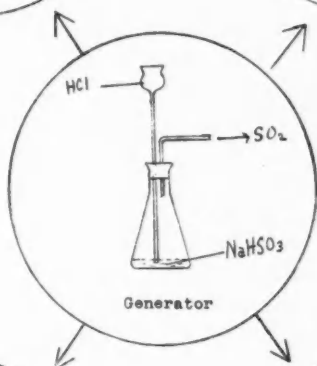
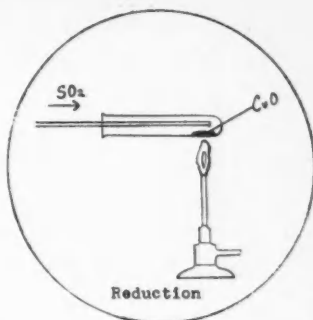
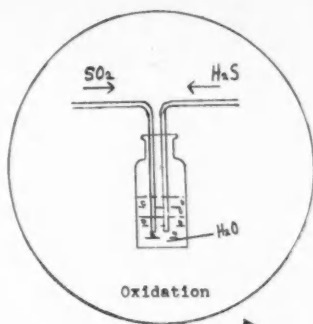
Incidentally, if you want to restore the red color to your apple, rub the skin with hydrogen peroxide. But don't eat it!

It Will Oxidize

Sulfur dioxide is not generally known as an oxidizing agent, but it will oxidize hydrogen sulfide, producing free sulfur:



You can demonstrate this reaction by bubbling sulfur dioxide through an aqueous solution of hydrogen sulfide. Or, if you wish, bubble both sulfur dioxide and hydrogen sulfide through water simultaneously. The



► VERSATILE sulfur dioxide plays many roles in the home laboratory theatre

hydrogen sulfide is prepared by adding dilute hydrochloric acid to iron sulfide.

It Will Reduce

Sulfur dioxide is better known as an active reducing agent. For example, it will reduce the oxides of many metals. Place a small quantity of cupric oxide in a dry test tube. With the tube in a horizontal posi-

tion, apply heat and allow sulfur dioxide to flow over the heated powder for a few minutes. Then remove and examine closely. Can you find any trace of metallic copper?

And It Will Affect You

Are your eyes smarting? Nose running? Throat burning? If so, you've had enough for a while. So let's get some fresh air and call it a day.



Chapter II

Experimenting With Colors

► WHAT A DULL and drab world this would be without color! Imagine everything in shades of black and white! Thanks to the chemist, our everyday life is surrounded by a riot of color. His various color creations in dyes,

inks and paints have made available to us a never-ending variety of color environment.

We shall prepare some of these colors as they are alone, as dyes, as inks and as paints.

1. Rainbow Colors

► VARIOUS CHEMICAL compounds have characteristic colors. We list here a few varieties of each color.

Red: (1) Add a few drops of sulfuric acid to a solution of potassium chromate. (2) Add a solution of ferric ammonium sulfate to a solution of sodium sulfocyanide. (3) Add a solution of potassium iodide to a solution of mercuric chloride. The solution is yellow at first, but will gradually turn to red.

Orange: Mix together solutions of sodium dichromate and sodium hydroxide. Add to this a solution of lead acetate.

Yellow: (1) Add a solution of sodium bisulfite (sodium hydrogen sulfite) to a solution of ferric ammonium sulfate. (2) Add a solution of lead acetate to a solution of potassium chromate.

Green: (1) Add sodium hydroxide solution to a solution of nickel chloride. (2) Add a few drops of ammonium hydroxide to a small quantity of

arsenious acid solution. *Careful — arsenious acid is very poisonous!* To this mixture, pour in a solution of copper sulfate. (3) Mix together in a beaker solutions of sodium dichromate, ferric chloride, lead acetate and potassium ferrocyanide.

Blue: (1) Add a dilute solution of potassium ferrocyanide to a dilute solution of ferric chloride. (2) Add ammonium hydroxide to a solution of copper sulfate.

Violet: (1) Dissolve crystals of iodine in carbon tetrachloride. (2) Dissolve potassium permanganate in water.

These are just a few colors that can be made rapidly for demonstration purposes. For a beautiful effect, make a full test tube of each color and stand them side by side in a rack.

To obtain some really intense colors, we must turn to organic chemistry. So the next few experiments will be devoted to the preparation of synthetic organic dyes.

2. Red Dye (Eosin)

► EOSIN (tetrabromofluorescein) is used as a dye, usually in the form of its sodium salt which is soluble in

water. To prepare it, shake one gram of fluorescein in six cc. of 95% alcohol. Carefully add, drop by drop,

about one-half cc. of bromine. (*Caution — very caustic! Do not spill on skin.*) The fluorescein will gradually dissolve to form first the soluble dibromofluorescein and finally the insoluble tetrabromofluorescein. If the latter is not precipitated, add a few additional drops of bromine. Pour the mixture into 15 cc. of water, stir and filter off the eosin. Suspend the crude eosin in water and add dilute sodium hydroxide solution until entirely dissolved. Now pour the solution into 10 cc. of boiling water to which one cc. of hydrochloric acid has been added. Finally, filter off the orange-red eosin.

To prepare the soluble sodium salt of eosin, mix thoroughly together in a mortar one gram of dry eosin with $\frac{1}{3}$ gram anhydrous sodium carbonate. Make into a paste with ethyl alcohol. Add one cc. of water, transfer to a test tube and heat gently until evolution of gas (CO_2) ceases. Then add five cc. ethyl alcohol, heat to boiling and filter the hot solution. Allow

the filtrate to stand. Eventually, green-red iridescent needles of the sodium salt will crystallize out of solution.

This is the commercial form of eosin which is used in red inks, as a dye for wool and silk, and as coloring for lipstick and nail polish.

As stated previously the sodium salt of eosin is soluble in water. The concentrated solution is deep brownish red whereas the dilute solution is yellowish-red with greenish fluorescence.

Note on Preparation of Bromine

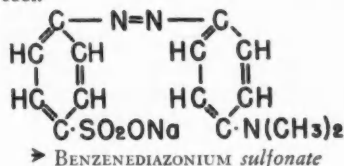
If you do not have bromine, the small amount needed for preparing eosin can easily be made. Simply mix together equal quantities (not more than one gram each) of potassium bromide and manganese dioxide in a test tube. Add one cc. of sulfuric acid and attach a delivery tube leading to another test tube immersed in a beaker of ice water. Heat gently. Bromine is liberated and will condense in the cool receiving tube. *Be very careful not to inhale the fumes or spill the liquid on the skin.*

3. Orange Dye (Methyl Orange)

► THE TECHNICAL name for methyl orange is sodium p-dimethylaminoazobenzene-sulfonate. (Hereafter, we will refer to it as "methyl orange"). It is formed by the diazotization of the amino group of sulfanilic acid and the coupling of the resultant products with dimethylaniline hydrochloride. But don't get discouraged; it really isn't as bad as it sounds. We shall proceed slowly, step by step.

First, thoroughly dissolve one gram of sodium carbonate in 25 cc. of water using a 100 or 150 cc. size beaker. Now add 3 grams of sulfanilic acid.

When the resultant effervescence ceases, warm the mixture until all solids are dissolved; then allow to cool.



In another container, dissolve one gram of sodium nitrite in 5 cc. of water. Add this to the sulfanilic acid solution. Stir and cool the liquid by

placing the beaker in a mixture of crushed ice, salt and water. Bring to a temperature of 5 degrees. Add to this, drop by drop, a solution of 4 cc. concentrated hydrochloric acid in 8 cc. of water. Stir after each addition and do not allow the temperature to rise above 10 degrees. You may accomplish this conveniently by using a thermometer to stir the liquid.

The above procedure is known as *diazotization*, which simply means the formation of diazonium salts. It seems that when nitrous acid acts upon the salts of aromatic primary amines, compounds with properties characteristic of ionic salts are formed. They have been termed "diazonium" salts because of their analogy to ammonium compounds. They are usually unstable and most of them are explosive in the dry state. For that reason, we are happy to oblige and keep them in aqueous surroundings. Because of their great activity, they find valuable use as intermediates in the preparation of many synthetic compounds and dyes.

In our experiment, the compound formed is benzenediazonium sulfonate. It is only sparingly soluble in water and will separate out as hydrochloric acid is added. After the acid has been added, let the solution stand for two or three minutes — no longer.

Mix together 2 cc. of dimethylaniline, 2 cc. of hydrochloric acid and 5 cc. of water. Cool and add to the cold diazonium salt solution. Stir rapidly and let stand for about five minutes. A deep red color should be formed. Upon adding a solution of sodium hydroxide (3 grams of NaOH in 10 cc. of water), methyl orange will

separate in fine orange crystals. Heat until a uniform orange color is formed. Add about 5 grams of salt and allow to cool. This will cause more complete precipitation of the methyl orange. The solution is now filtered, and the precipitate purified by dissolving in hot water and recrystallizing.

Coupling

This latter portion of our experiment is known as *coupling*, which is the reaction of a diazonium salt with an amine, in this case, dimethylaniline. In other words, coupling occurs between benzenediazonium sulfonate and dimethylaniline with the resultant formation of *p*-dimethylaminoazobenzene-*p*-sulfonic acid. The addition of sodium hydroxide converts the acid into the sodium salt, methyl orange.

If your solution turns dark green instead of orange, it is probably due to the formation of *p*-nitrosodimethylaniline. This compound is formed when an excess of nitrous acid is used and is insoluble in water. However, when warmed with sodium hydroxide it is converted into the soluble *p*-nitrosophenol. Thus you may still obtain methyl orange by allowing the solution to cool and filtering off the precipitate. It will be necessary to repeat the process several times. The precipitate is then purified as before.

Methyl orange is used as an indicator. Dissolve a small amount of it in warm water. Add a small quantity of hydrochloric acid and a lovely red color appears. With alkali solutions, the indicator turns yellow.

Although it forms a beautiful orange color, methyl orange is not used as a dye because of its sensitivity to acids and alkalis.

4. Yellow Dye (Naphthol Yellow)

► WHEN bituminous or soft coal is heated to a high temperature in a sealed retort a thick, tarry black liquid condenses which is known as *coal tar*. Perhaps you have heard of it.

When the coal tar is distilled, a number of important compounds are obtained. Included in the fraction which distils over from 110° to 205° is an acid oil and crude naphthalene. As this mixture cools, the naphthalene crystallizes out and is removed and purified.

Now when naphthalene is sulfonated (treated with sulfuric acid) at 0°, a compound known as *a*-naphthalene-sulfonic acid is obtained. The sodium salt of this acid is fused with sodium hydroxide to form *a*-naphthol. When *a*-naphthol is sulfonated and then nitrated a compound known technically as 2, 4-dinitro-1-naphthol-7-sulfonic acid, more commonly known as *naphthol yellow*, is obtained.

So, there you have it. Simply obtain a piece of soft coal and get to work!

But for those who do not wish to go all the way back to the coal (including us), we suggest using *a*-naphthol as the starting point. Obtain a good grade of said chemical, and place 2 grams of it in a small flask. Add to this 5 cc. of concentrated sulfuric acid. Heat the mixture by immersing the flask in a larger container of boiling water. Keep the water boiling vigorously. The mixture in the flask should attain a temperature of 120°. Continue heating for 15 minutes; then cool and pour the contents

into 15 cc. of water in a beaker. The first step of sulfonation is now completed.

Next we proceed to the nitration process. Cool the solution to around 25° by immersing the beaker in cold water. During the nitration process, it is essential that the temperature of the liquid does not rise above 40°. It might be advisable to add a little ice to the water in which the beaker is immersed. Now add to the mixture 3 cc. of concentrated nitric acid, *a few drops at a time*. Stir the solution vigorously during the addition of the acid. This is rather tiresome, and if you have a mechanical stirrer, it certainly will be useful here. After all nitric acid has been added, continue stirring for about 30 minutes. Then allow the solution to stand for 24 hours while you recuperate.

After a day or so, naphthol yellow will crystallize out of the solution. Now you can either extract the acid as is, or you can prepare the potassium salt in which form it is available commercially.

To obtain the acid, carefully pour off the liquid and transfer the crystals to another container of water. Heat to boiling for a few minutes, then filter. The deep intense yellow solution of naphthol yellow is obtained as the filtrate.

To obtain the potassium salt, separate the crystals by filtration. Wash them with a small quantity of saturated sodium chloride solution. The crystals are then dissolved in the smallest possible quantity of hot water. Next prepare a concentrated solu-

tion of potassium carbonate and add it to the hot naphthol yellow until the solution just barely reacts alkaline with litmus. The orange-yellow crystals of the potassium salt will separate

out on cooling. They can be filtered off and dried.

Naphthol yellow is used for dyeing wool and silk; for coloring foods and cosmetics.

5. Green Dye (Malachite Green)

► FOR THE synthesis of Malachite green, we need 3 cc. of *freshly distilled* benzaldehyde. Use care in performing this distillation. It might be a good idea to add a few pieces of porcelain plate or glass beads to the benzaldehyde in order to prevent "bumping" and uneven boiling.

Next we must prepare *anhydrous* zinc chloride. Place 5 grams of the compound in a large porcelain evaporating dish. Heat gently at first with constant stirring. Gradually apply more heat and finally enough to melt the compound. Continue to heat for a few minutes, then cover the dish with a glass plate and allow to cool. Add to the cooled zinc chloride, the 3 cc. of freshly distilled benzaldehyde prepared above along with 6 cc. of dimethyl aniline. Heat the mixture on the steam bath for 90 minutes.

You can devise your own "steam bath" by using a large beaker on which the evaporating dish can set comfortably, on top, without falling in. Fill the beaker half full of water and heat. The steam from the boiling water will heat the dish. Of course, arrange the dish so that the lip of the beaker remains open to allow excess steam to escape. Cover the evaporating dish with a glass plate. Stir the contents frequently during the heating and if the mixture becomes thick, add a little hot water.

The product we obtain is known as the *leuco-base* of Malachite green,

or, if you prefer, tetramethyldiaminotriphenylmethane. Our next step is to convert it to the carbinol (color) base by oxidation.

Dissolve the residue in a solution of 3 cc. hydrochloric acid and 6 cc. of water. Transfer the liquid to a large beaker. Add 100 cc. of water and about 20 grams of cracked ice. Now prepare a suspension of lead dioxide, PbO_2 , by vigorously shaking 2 grams of the powder in 15 cc. of water. This is our oxidizing agent. Add it to the beaker slowly, in small portions, stirring continuously.

The next step is to remove the lead. This is done by adding a solution of 2 grams of sodium sulfate in 10 cc. of water. Filter off the resultant lead sulfate.

Malachite green is usually precipitated as the double salt of the hydrochloride and zinc chloride.

Add to the filtrate a solution of 3 grams zinc chloride dissolved in 15 cc. of water followed by 12 grams of solid sodium chloride. Stir thoroughly for a few minutes. Filter off the green crystals and carefully dry. If you have worked carefully, you should have a yield of about 3 grams.

Prepare to Dye

Now that you have obtained Malachite green, are you prepared to dye?

Prepare a solution of Malachite green by dissolving a small quantity of the powder in water. Heat to boil-

ing and immerse a piece of wool or silk in the hot solution for several minutes. Remove and wash with water. The cloth is dyed a deep blue-green. This process is known as *direct dyeing*.

As you have certainly observed by now, the dye is an intense blue-green color—and a little goes a long way. It is a basic dye and will dye wool and silk directly. However, in order to dye cotton, the cloth must be mordanted first. By "mordanted" we mean treated with a substance ("mordant") which is taken up by the fibers of the cloth. The mordant in turn takes up the dye. Thus I suppose you could say that we actually dye the mordant, not the cloth. But who knows the difference?

The Mordant Process

If you will perform the above operation with cotton you will find the color is not fast. To dye cotton preliminary treatment with a mordant is necessary. This process is known as *mordant dyeing*. (For best results with cotton, it is advisable to boil it for 10 minutes in a solution of one gram sodium carbonate in 500 cc. of

water then rinse several times in clear water, before attempting to treat it.) Dissolve a very small quantity of tannic acid (about 0.2g.) in 100 cc. of water. Heat to boiling and immerse a piece of cotton cloth in the hot solution for several minutes. Remove the cloth, press it with a spoon to remove excess liquid, then immerse for several minutes in boiling Malachite green solution. You will note this time that the dye is fast. To make the color somewhat darker, the tannic acid may be fixed to adhere more strongly to the fibers. This is done by dipping the cloth in tannic acid as before and then immersing in a solution of tartar emetic for about 10 minutes. Use about 0.2 g. of tartar emetic dissolved in 200 c. of water.

Malachite green is converted into a colorless compound by reducing agents. This can be demonstrated by adding a solution of sodium bisulfite to the dye. Incidentally, this is a good method of removing the dye from your glassware . . . (or from your hands?)

Well, we hope you have enjoyed dyeing. If so, we must dye again some time.

6. Blue Dye (Methylene Blue)

➤ THE PREPARATION of Methylene Blue presents a mild challenge to the home chemist. Although rather involved, the preparation should present no great difficulty if instructions are carefully followed. In order to facilitate matters, the process has been broken down into separate steps in real "do-it-yourself" fashion. You can check off each step as it is completed. Again, we stress that instructions be followed most carefully. Particular at-

tention should be paid to quantities used and temperatures designated.

□ 1. The first step involves the preparation of starch-iodide paper which will be needed to test the reaction. Mix about 2 grams of ordinary starch with about 25 cc. of water in a mortar. Grind the mixture with the mortar until a smooth suspension is obtained — free from lumps. Pour the mixture slowly, with stirring, into 200 cc. of boiling water. Stir for a

few minutes and allow to cool. When cool, mix a portion of this solution with an equal quantity of potassium iodide solution. Soak several sheets of filter paper in this mixture for a few minutes, then allow to dry.

□ 2. Preparation of nitrosodimethylaniline. Dissolve 5 cc. of dimethylaniline in 12 cc. of concentrated hydrochloric acid. Add 25 grams of cracked ice to the solution and insert a thermometer. Stir until the temperature reaches 0 deg. Dissolve $2\frac{1}{2}$ grams of sodium nitrite in 10 cc. of water. Slowly add this solution to the iced mixture, a few drops at a time. Stir rapidly after each addition. Do *not* allow the temperature to rise above 5 deg. during this addition. If necessary, more ice may be added to keep the temperature down. The mixture will turn yellow immediately and will gradually darken to a deep orange. After all the nitrite has been added, withdraw a small sample of the liquid and dilute it with 3 volumes of water. Test this solution with the starch-iodide paper prepared in step 1. The test should indicate the presence of free nitrous acid, which will color the paper blue. If the test is negative, more nitrite solution must be added until the blue color is obtained. Proceed exactly as outlined above; add only a small quantity of nitrite, then test again. Remember to keep the temperature below 5 deg. This is important!

After a positive test reaction is obtained, the entire solution is allowed to stand for two hours. At the end of this time, yellow crystals of nitrosodimethylaniline will separate out.

□ 3. Preparation of p-aminodimethylaniline. Our next reaction con-

sists of reducing the nitrosodimethylaniline mixture. Stir the latter vigorously and add 25 cc. of water. Start the reduction process by adding 20 cc. of concentrated hydrochloric acid and 5 grams of iron filings. This time it is necessary to keep the temperature below 30 degrees. So add sufficient cracked ice to maintain this temperature. Stirring frequently, allow the solution to stand for a short while. After this time, extract a few drops of the solution with a medicine dropper and allow a drop to fall onto a clean piece of filter paper. When the spot on the filter paper is colorless, the reduction is complete. If your spot is yellow, then continue the reaction. If necessary, more iron filings and hydrochloric acid may be added. Continue to test from time to time until the solution does not color the filter paper.

□ 4. Neutralization is next. Partially neutralize the solution with calcium oxide, or lime, then finish the job with precipitated chalk (calcium carbonate). The carbonate is added, a small quantity at a time, with stirring after each addition, until all frothing ceases. Finally, filter off all the lime, carbonate and iron filings. Keep the clear filtrate.

□ 5. The following several steps are performed quickly one after the other. In order to be ready it might be a good idea to prepare the solutions needed in advance, as follows: Solution A — Dissolve $8\frac{1}{2}$ grams of sodium thiosulfate in 10 cc. of water. Solution B — Dissolve 13 grams of potassium bichromate in 30 cc. of water. Solution C — Dissolve 4 cc. of dimethylaniline in 6 cc. of concentrated hydrochloric acid. Solution D

— Dissolve $\frac{1}{2}$ gram copper sulfate in 5 cc. of water. If necessary, the solutions may be heated to completely dissolve the solids, but be sure to cool again before using.

□ 6. Shake the clear filtrate from step 4 vigorously. Add solution A (sodium thiosulfate), shake again, and proceed immediately to next step.

□ 7. Add one-half of Solution B (potassium bichromate) in small portions over a period of several minutes. Shake after each addition. Allow the mixture to stand for an additional two minutes before proceeding to the next step.

□ 8. Add all of Solution C (dimethylaniline), shake, and proceed immediately to next step.

□ 9. Add the second half of Solution B (potassium bichromate), again in small portions over a period of several minutes. This time, continue stirring and shaking the solution for an additional five minutes before proceeding to the next step.

□ 10. Add Solution D (copper sulfate) and shake again.

□ 11. Transfer the mixture to a large flask and apply gentle heat. Gradually increase the heat until the

mixture just begins to boil. You will note the mixture takes on a bronze copper-like appearance. If excessive frothing occurs, discontinue heating until it settles down, then re-heat. You may have to repeat this several times before the liquid boils.

□ 12. The hot solution is now filtered. The black precipitate is washed with hot water. By now you will notice that the filtrate is an intense blue color. This is due, of course, to the methylene blue. To separate it, proceed to the next step.

□ 13. Heat the filtrate to 80 degrees. For each 25 cc. of solution you have, add 4 grams of common salt and $2\frac{1}{2}$ cc. of hydrochloric acid. Allow the solution to cool. Methylene blue will separate in fine crystals.

Methylene blue is a type of *thiazine* dye. It is a beautiful shade of blue and is used for dyeing cotton. It is also used as a stain in bacteriology.

We seem to have arrived at exactly 13 steps for this experiment. This will never do. So to break the spell, suppose we add another step:

□ 14. Wash the glassware and clean up the mess.

7. Violet Dye (Methyl Violet)

➤ METHYL VIOLET is another dye obtained from the black, sticky, foul-smelling coal tar. From the coal tar we obtain benzene. Subjecting the benzene to nitration, we obtain nitrobenzene. The nitrobenzene is reduced to form aniline. And from aniline and its derivatives we obtain a multitude of dyes — all colors of the rainbow in various shades and hues. One of these derivatives is *dimethylaniline*, which

we will use in preparing methyl violet. Dimethylaniline is prepared by heating aniline, methanol and sulfuric acid under pressure.

We will use dimethylaniline as our starting point.

Methyl violet is formed by heating phenol and dimethylaniline with sodium chloride and cupric sulfate. Mix 65 grams of finely powdered sodium chloride with 5 grams of finely pow-

dered cupric sulfate. Common table salt may be used if it is pulverized by grinding in a mortar. The cupric sulfate should also be ground in a mortar. Sift the thoroughly mixed powders into a large dry beaker.

Next, prepare a solution of phenol (carbolic acid) by adding 4 grams of the reagent to 15 cc. of water. (Do not allow phenol to come in contact with your skin as it can cause a serious burn.) As all of the phenol will not dissolve in this quantity of water, just heat the solution until the solid crystals melt. Pour into the beaker containing the mixed salt and cupric sulfate, stirring constantly. You will end up with a light green watery paste. To this add 10 cc. of dimethylaniline and continue to stir. Transfer the mass to a large Florence flask and heat to a temperature of 60 degrees. Keep the solution at this temperature for three hours or longer.

By now you will begin to observe the violet coloration as methyl violet is formed in the solution. Allow the mixture to cool and then transfer the

mass (or should we say mess?) to 300 cc. of boiling water to which 4 grams of calcium oxide has been added. Allow this mixture to boil until it is fairly free from lumps — about one half hour — and allow to cool. The dye separates out of solution as a dark greenish-purple mass. Transfer a small portion of it to some alcohol in a beaker. The lovely shade of violet is indicative of methyl violet.

The violet color of the dye is quite intense. You can dilute the alcohol solution many times and the purple color will still be present.

Methyl violet is used in certain inks and for dyeing wool, silk, and mordanted cotton. It is not fast to light.

Crystal violet, similar to methyl violet but less reddish in color, is prepared by heating Michler's ketone (4,4'-Bis-dimethylamino-benzophenone) with dimethylaniline and phosphorous oxychloride. This compound mixed with methyl violet forms the mixed with methyl violet forms *Gentian violet*, used as an antiseptic.

8. Inks

► NOWADAYS the manufacture of ink is a highly specialized industry. We have inks that write under water, washable inks, permanent inks, wet inks that write dry, dry inks that write wet, and hundreds of other types. The inks we describe here are not the modern specialized types. But, they will serve well for all practical purposes.

Blue Ink

Prussian blue (ferric ferrocyanide) provides the coloring pigment for this

ink. Dissolve 1 gram of ferric ammonium sulfate in 10 cc. of water. Dissolve 2 grams of potassium or sodium ferrocyanide in 15 cc. of water. Mix the two solutions, filter and thoroughly wash the precipitate. Then add just enough oxalic acid solution to dissolve the precipitate forming a syrupy liquid. Finally, thin with water and your ink is ready for writing.

A dilute solution of Prussian Blue in oxalic acid is also used as laundry bluing.

Black Ink

The color for our black ink is derived from the reaction of ferrous sulfate on nutgalls. Nutgalls are obtained from the twigs of various species of *Quercus* which grow in Asia Minor. Nutgalls are comprised chiefly of tannic acid, with a smaller percentage of gallic acid, ellagic acids and resin.

Boil 7 grams of nutgalls in 30 cc. of water for at least one hour. Add water as necessary to replenish that lost by evaporation. Filter the solution and while still hot, add 2 grams of ferrous sulfate and 1 gram of gum arabic. Heat again to dissolve all solids, and then filter once more.

Red Ink

The color here is obtained from the dried bodies of insects. Cochineal, *Coccus Cacti*, is found in Central America and Mexico. The dried female insect with the young larvae is used. Chemically it consists of carminic acid, coccerin, and fat.

Place 2 grams of cochineal in 20 cc. of water and heat to boiling, shaking occasionally. Then remove from the flame and allow to cool thoroughly, stirring frequently. When cold, add a

solution of 2 cc. ammonium hydroxide in 6 cc. of water. Allow to stand overnight; then filter.

Green Ink

Dissolve 5 grams of copper acetate and 3 grams of potassium bitartrate in 20 cc. of water. Allow the solution to boil gently over a low flame for about 30 minutes. Then filter. If too thick, add a small quantity of water.

Purple Ink

We have used twig growths and dried insects; now we shall use wood chips. Logwood or hematoxylon is the heartwood of a Central American tree of the senna family. It contains about 10% hematoxylon with some tannin and resin.

Boil 3 grams of logwood in 12 cc. of water until the solution is colored deep red. Then add 3 grams of aluminum sulfate. Boil again for about 10 minutes and while still hot, add 1 gram of gum arabic. Finally, filter the solution.

Commercially, aniline dyes are replacing the natural dyes in most inks. But, perhaps you will find it interesting to prepare the inks by the old-fashioned "natural" method, just for fun.

9. Sympathetic Inks

➤ ALTHOUGH sympathetic or "invisible" inks serve very little practical purpose, they make interesting experiments for the home lab.

Most sympathetic inks are brought out by heat. The writing is made on a piece of paper and allowed to dry. The paper is then heated and the invisible writing suddenly appears. With some inks, the paper must be

quite hot, and you must be careful not to set it afire.

A solution of cobalt chloride forms a sympathetic ink which turns a beautiful green when heated, but will gradually disappear again when the paper is cooled.

Mix together equal quantities of copper sulfate and ammonium chloride solutions. When you write with

this solution and heat the paper, the writing will appear in yellow characters.

A solution of potassium nitrate makes a sympathetic ink that turns brown upon heating. Here it is necessary to slightly scorch the paper to make the ink visible.

Another type of sympathetic ink depends upon reaction with a chemical to become visible. In this case, writing is done with one chemical.

After it is dry, the writing is wiped with the solution of a second chemical. For example, write with a dilute solution of potassium ferrocyanide. When dry, spread a solution of copper sulfate over the writing with a soft brush. The writing will be visible in red characters.

Or, you can write with copper sulfate solution and spread ammonium hydroxide over it. Blue writing will appear.

10. Paint

► ORDINARY PAINT consists of two general components: the *pigment*, which contains the coloring matter, and the *vehicle*, an oil in which the pigment is suspended. Of course, various other substances are added to obtain specific properties. Sometimes a *filler* (such as silica, kaolin, barium sulfate, or calcium carbonate) is added to give greater bulk and decrease the cost. A *drier* is added to hasten the drying process. The substance is usually the water-insoluble soap of cobalt, manganese or lead. Finally, a *thinner* must be included to obtain proper consistency for easier application.

Most manufacturers list the essential ingredients of their paint on the label. For example, we found a can of exterior green house paint in the cellar with the following analysis:

Pigment 37.7%:-

Chrome Green - - - 75.0%
Magnesium Silicate - - 25.0%

Vehicle 62.3%:-

Linseed Alkyd Resin - 50.0%
Driers - - - - - 1.7%
Mineral Spirits - - - 48.3%

This paint was further tinted with

chrome yellow and titanium dioxide to obtain the desired shade.

A can of inside semi-gloss white enamel had the following composition:

Pigment 51%:-

Titanium Oxide - - - 51%
Calcium Carbonate - - 41%
Silicates - - - - - 3%
Zinc Oxide - - - - - 5%

Vehicle 49%:-

Soya/Linseed Alk. Resin - 43%
Drier - - - - - 5%
Aliphatic Hydrocarbons - 52%

And, finally, an exterior White Lead paint:

Pigment 72.2%:-

Basic Lead Carbonate - - 100%
Vehicle 27.8%:-

Linseed Oil - - - - - 72%
Mineral Spirits - - - - 23%
Liquid Drier - - - - - 5%

Note that the green paint employs magnesium silicate as the filler or "body," while the inside enamel uses calcium carbonate and the white lead paint contains only one compound which acts as coloring matter, filler and body. The vehicle in all cases is linseed oil or the newer linseed alkyd

resins. The latter consist of alkyd resins (such as those made from glycerol and phthalic anhydride) modified with linoleic acid, which is present in linseed oil as a glyceride. They tend to make a rapid-drying paint with a durable finish. The thinner in most modern paints is usually a petroleum fractionation product, such as mineral spirits.

You can make a small quantity of paint in the laboratory by grinding together the pigment (see below) with linseed oil to form a smooth, syrupy paste. The most difficult part will be to obtain a really smooth mixture free of small particles. The product is then diluted with turpentine to the desired consistency.

The pigment is prepared by mixing together the proper solutions and filtering off the resultant precipitate. The precipitate is scraped off, transferred to a metal or glass container, and carefully dried over gentle heat. In the following descriptions, the compounds are simply designated as "solutions." The strength of these solutions is entirely up to you and depends on how much pigment you care to prepare. Usually one gram in 10 cc. of water makes an average strength solution. Be sure all solids are thoroughly dissolved before mixing the solutions. Use heat if necessary.

Yellow:

Mix sodium dichromate solution with an equal quantity of lead acetate solution. This is *chrome yellow*.

Another yellow pigment — "orpiment" — can be made by passing a stream of hydrogen sulfide gas through a solution of arsenious acid (*careful—very poisonous*) to which a

few drops of hydrochloric acid have been added.

Blue:

A solution of ferric chloride is mixed with a solution of potassium ferrocyanide. The deep blue pigment is known as "Prussian Blue."

If you prefer a lighter shade of blue, add ferrous sulfate solution to the potassium ferrocyanide. This pigment is commonly called "Turnbull's Blue."

Green:

We learned in school that yellow plus blue equals green. Hence to obtain a green color we shall mix Chrome Yellow with Prussian Blue. Mix together a solution of sodium dichromate with a solution of ferric chloride. In another vessel mix together solutions of lead acetate and potassium ferrocyanide. Finally, combine the two mixtures. This pigment is sometimes sold as "chrome green."

Actually, chrome green pigment is pure chrome oxide prepared by igniting ammonium bichromate. Heat the compound in a dry metal pan. The crystals will suddenly flare up and chromic oxide is formed in the midst of a sparkling pyrotechnic display. (Keep your face away!).

Orange:

"Chrome orange" pigment is prepared by mixing together solutions of sodium dichromate and sodium hydroxide, and then adding a solution of lead acetate.

Red:

Vermilion is a brilliant red pigment. It is mercuric sulfide and is prepared by bubbling hydrogen sulfide into a solution of mercuric chloride.

The resultant black precipitate is filtered off and heated until it turns red.

Iron oxide forms a reddish-brown pigment. Mix together solutions of ferric chloride and ammonium hydroxide.

White Lead:

This popular white pigment can be made in the laboratory by mixing a solution of lead acetate with a smaller quantity of sodium carbonate solution.

Of course these are only a very few of the many pigments available. In addition to these are many "tinting" pigments which are used with white pigments to obtain various shades of ivory, cream, grey, etc. Some examples are:

Lampblack—carbon.

Raw Umber—Hydrated ferric oxide with manganese dioxide.

Burnt Umber—Calcined raw umber.

Raw Sienna—Hydrated ferric oxide with a smaller quantity of manganese dioxide.

Burnt Sienna—Calcined raw sienna.

As in other chemical industries, the paint industry is constantly changing and improving. Instead of the former white-lead linseed oil turpentine type of paint we now have the titanium dioxide-soya alkyd resin-aliphatic hydrocarbon type. This is just another example of the almost routine role that chemistry is constantly playing to improve the products we use.



Chapter III

Experimenting With Fire

➤ BY FAR, the most popular experiments for the home chemist are those dealing with fiery and spectacular reactions. A display of fireworks never fails to awe, and a fiery reaction never fails to mystify.

But, it must be remembered, these experiments are also somewhat dangerous to perform. In his enthusiasm to make bigger and better fires, the

home chemist sometimes grows careless and ignores the common safety rules. Fires are best ignited outdoors or on the cellar floor where there is no danger of fire from flying sparks. Keep your face away from all reactions until you are positively sure all reaction has been completed. *Use only small quantities.*

1. Fireworks

➤ FIREWORKS should be set off outside unless you use very small quantities and do not object to irritating smoke. Best results are obtained on dark, wind still evenings.

All ingredients used must be dry and finely powdered. Powdering should be done in a mortar — *each ingredient separately!* The powders are mixed together on a sheet of paper by lightly shuffling with a knife or spatula.

The mixed powders are ignited easily by using touch paper. The latter is made by soaking sheets of filter paper in concentrated potassium nitrate solution. When dry, they are cut into thin strips.

Remember the composition of all the following mixtures is given by parts — not by weights. We suggest that you refrain from using too large quantities.

And finally, the mixtures must be made immediately before using for best results. Do not store any powders.

Colored Fires

Thoroughly mix the ingredients and pour into a metal pan—a metal screw cap jar lid will be satisfactory. Form a neat pile and ignite with touch paper.

White

- 6 parts—potassium nitrate
- 1 part—sulfur
- 1 part—antimony sulfide

Red

- 5 parts—strontium nitrate
- 1 part—sulfur
- 1 part—charcoal, powdered
- 3 parts—potassium nitrate

Yellow

- 3 parts—sodium chloride
- 4 parts—potassium nitrate
- 1 part—sulfur
- 2 parts—powdered charcoal

Green

- 7 parts—barium nitrate
- 2 parts—sulfur
- 4 parts—potassium nitrate
- 1 part—powdered charcoal

Serpent's Eggs

Thoroughly mix together 3 parts potassium nitrate, 5 parts sugar, and 5 parts potassium bichromate. Form a paste with alcohol and mold into pellets. When dry, ignite with touch paper. A bulky snake-like ash is formed.

Flower Pot

Mix together 1 part each of powdered magnesium, powdered iron, charcoal, and sulfur; $\frac{1}{2}$ part of powdered zinc, and 2 parts of potassium nitrate. Now obtain a small iron crucible and drill a small hole in the bottom of it. Insert a strip of touch paper through the hole, extending about $\frac{1}{2}$ inch into the crucible. This will serve as a fuse. Holding your finger over the hole, pour in the mixed powders, until the crucible is about $\frac{1}{4}$ full. Then wedge the mixture in with a piece of cardboard and

invert the crucible. Ignite the touch paper, step back and witness a brilliant display. The flower pot must be ignited outside, as the flying sparks will attain considerable height.

Sparklers

A mixture of 20 parts potassium nitrate, 6 parts sulfur and one part charcoal is blended together with gum arabic solution to form a thick paste. Obtain several lengths of thin wire strips and dip them into the paste. When dry, ignite with a match.

All-Star Sparkling Fire

Mix together 1 part each of powdered magnesium, powdered iron, charcoal, sulfur, powdered zinc, antimony sulfide, lycopodium powder, cloves, ginger, cinnamon, sugar, and 3 parts potassium nitrate. Ignite outside with touch paper.

2. Spectacular Reactions

► PLACE A DROP of glycerin in a metal pan. Sprinkle a "pinch" of finely powdered potassium permanganate on top of it. Then, wait. Soon the mixture starts to smolder and suddenly will ignite itself, burning with a blue flame.

Prepare a mixture of one gram of ammonium nitrate and 0.1 gram (a "pinch") of ammonium chloride. Place the mixture in a small metal pan or lid. Sprinkle evenly over the top of it, two grams powdered zinc. Now to start the reaction, add one drop of water. At first nothing happens. Gradually smoke will appear and the mixture will burst into a

brilliant green flame. Keep your face away!

Place one or two grams of ordinary cane sugar in an evaporating dish. Add a little concentrated sulfuric acid and warm the mixture *gently*. The sugar will become charred and will swell up to a large voluminous mass as a number of gases are evolved.

Heat a few crystals of ammonium bichromate in a pan. The crystals will burst into a sparkling flame and a green mass of chromium oxide remains.

Carefully mix together 5 cc. of con. sulfuric acid and 6 cc. of con. nitric acid. Cool the solution, then soak a

small tuft of cotton in it for ten minutes. Remove the cotton, wash thoroughly with warm water, and allow to dry. When dry, bring it to a flame. It burns rapidly with a brilliant flash of light. This is gun-cotton.

To eight cc. of con. potassium bichromate solution, carefully add two cc. of con. sulfuric acid. The solution becomes quite hot. When cool, small red crystals of chromic acid will separate out. Carefully pour off the liquid, scrape the crystals out and allow them to dry in a porcelain evaporating dish. Do not touch them with your bare hands. When dry, allow a few drops of alcohol to fall upon them. They will burn with a brilliant flash of light.

Place one or two grams of potassium nitrate in a dry hard-glass test

tube. Heat the powder evenly until it is entirely molten. Then drop a few particles of antimony sulfide into the tube. As each particle reaches the nitrate it burns with a brilliant white light. Using fresh potassium nitrate, repeat the experiment and add sulfur to the molten nitrate. The sulfur burns with a bright flame. Remove the tube from the flame before adding the sulfur. Sometimes the heat is sufficient to melt the glass, so it is wise to hold the tube over a metal pan full of sand as a precaution.

Mix together two parts of zinc with one part of sulfur. Throw the mixture onto a hot metal pan or plate. The mixture burns violently with a green flame. Be sure to keep your face away!

3. Phosphorus – Spontaneous Combustion

➤ PHOSPHORUS is one of the most interesting of all the elements. Its peculiar property of glowing in the dark places it in a special and rare category. For some unexplained reason, man has always been intrigued by any substance with phosphorescent properties.

The history of phosphorus is no less interesting than the element itself. It was first prepared in 1669 by a German alchemist, Hennig Brand. Brand, like every other alchemist of his day, was searching for the elusive philosopher's stone. We can never tell you what gave him the idea that this magic stone would be found in human urine, but, nevertheless, he carried on a series of elaborate experiments with

urine. After much experimentation, he obtained a yellowish waxy substance by distilling a residue from the urine. We can imagine how thrilled he must have been when he noticed that this strange substance glowed in the dark!

Brand kept the details of the preparation of this strange substance secret, but the news soon leaked out. He then sold his formula to other chemists, who also made the element in secret. It was not until 1737 that the method of isolating phosphorus was made known to the world in general. It was soon discovered that the element could be obtained from bones, and the unpleasant method of obtaining it from urine could be abandoned.

It is truly remarkable that Brand could prepare phosphorus with the very limited equipment and knowledge then available. Even today with all of our modern equipment, phosphorus is not isolated with ease.

Words of Caution:

We do not recommend these experiments for the careless or the inexperienced. Phosphorus may be fascinating, but it is also intensely poisonous. It should *never* be allowed to touch the skin, as it causes painful burns which are extremely difficult to heal. Always handle with forceps and keep it under water when not in use. Do not inhale its vapors. You will note that phosphorus has a garlic-like odor. But do not "note" too strongly—these fumes are poisonous too.

Yellow Phosphorus

Phosphorus occurs in three allotropic forms: yellow, violet, and black. However, the two most common forms are yellow and red. There is a difference of opinion as to whether the red form is a separate allotropic modification. One of the latest theories is that red phosphorus is phosphorus only partially changed from the yellow to the violet form.

The phosphorus obtained by the reduction of phosphates is always the yellow variety. This is "regular" phosphorus and the other allotropic forms are prepared from it.

Place a piece of yellow phosphorus the size of a pea in a flask half filled with water. Apply gentle heat. The phosphorus quickly melts under the warm water. Now stopper the flask; shake, and cool under running water. The phosphorus separates into many small globules. You will find these

small balls handy for experimenting.

Phosphorus combines readily with oxygen and ignites in the air at 30 degrees. Take a small piece and dry carefully with filter paper. Note the white fumes as the element starts to react. Place in a metal dish and heat very gently. Almost immediately it will ignite and burn with a bright yellow flame accompanied by dense white smoke (P_4O_6 and P_4O_{10}).

Spontaneous Combustion

Phosphorus is very soluble in carbon disulfide. Dissolve a piece about the size of a rice grain in 3 cc. of carbon disulfide. Dip a piece of filter paper in this solution (with forceps), and hold it suspended in the air. Nothing happens at first. But, wait. Suddenly the paper ignites with a flash of greenish flame. The filter paper is not consumed, but only partially charred.

If you want to write your initials in flames, you can do so by painting them on a large piece of filter paper with the phosphorus solution. Use a small paint brush for this purpose. Again hold the paper in mid air with forceps. Suddenly the outline of your initials will burst into flame.

And It Glows In The Dark!

Perhaps you would prefer your initials in luminous characters instead of flames. If so, paint your initials with the phosphorus solution as before, but on a white card instead of filter paper. Place the card in total blackness and observe the luminous writing.

Be very careful with the phosphorus solution, as it is highly flammable. Dispose of it immediately after experimenting either by burning it or

washing it down the drain with large quantities of water.

Place a small piece of phosphorus in a flask and cover with water. Attach a one-hole stopper containing a small glass tube extending about 3 inches above the flask. Boil the water in a dark room. If the room is dark enough, you will be able to observe the rather eerie effect of luminous steam.

Red Phosphorus

Red phosphorus is so unlike yellow phosphorus, it is difficult to realize both forms are the same element. The red type is an amorphous powder. It will not ignite spontaneously. It will not dissolve in carbon disulfide. It will not glow in the dark. It has no odor and is not poisonous. It ignites only when heated to about 240 degrees. You can prove this if you wish by placing some of the powder in a metal pan and heating. Compare the amount of heat you must apply with that applied to yellow phosphorus in order to ignite the powder.

Red phosphorus is prepared by

heating yellow phosphorus in the absence of air. The action may be catalyzed by a trace of iodine.

Violet phosphorus is prepared by dissolving phosphorus in molten lead and then allowing it to separate by crystallization.

Black phosphorus is made by subjecting yellow or red phosphorus to 4000 atmospheres of pressure at a high temperature.

The yellow phosphorus can be prepared from any other form by distillation. When heated strongly enough, all forms of phosphorus vaporize and this vapor always condenses to form the yellow variety.

We suggest that you do not attempt to prepare the various allotropic modifications of phosphorus. These reactions are a little too dangerous for the home laboratory.

When you are through experimenting, be doubly sure that you have thoroughly disposed of all phosphorus particles or solutions. Ignite any stray particles and thoroughly wash all equipment.



Chapter IV

Experimenting With Metals

► NATURE has supplied us with numerous metals exhibiting a wide variety of properties. Considering melting points, they range from mercury, which has such a low melting point that it is liquid at ordinary temperatures, to tungsten which melts at a temperature of 3380 deg. C.! Or, considering activity, platinum will resist corrosion by even the strongest acids and yet potassium corrodes so rapidly in the air that it must be preserved under oil! In weight, they vary from lithium, with an atomic weight of

6.940 to uranium with an atomic weight of 238.07. Some are extremely hard; others are so soft they can be worked like putty.

It is not feasible to examine every single metal. So we have selected a number with different properties to investigate. We have tried to provide a brief history of the metals and their development; we will examine their properties and, where possible, isolate them from their compounds. And finally, we will examine the compounds themselves.

1. Silver

► SILVER has been known and sought after for many centuries and was once considered more valuable than gold. Today gold is more valuable, but silver is far more useful. It is the best conductor of heat and electricity known and is one of the most malleable and ductile of all metals. Alloys of silver are used extensively to make coins, jewelry, tableware, etc.

The Metal

It is possible to obtain silver in the pure state from an alloy by chemical means in a fascinating home experiment. Place 10 cc. of dilute nitric acid in a flask and add a dime or a quarter, depending on your financial status. Heat the flask gently until the entire coin is dissolved, being careful not to inhale the brown fumes. The solution is colored blue by the copper in the coin, and consists primarily of

copper nitrate and silver nitrate. Add an equal quantity of water, mix thoroughly and pour one-half of the mixture in an evaporating dish. Save the other half of the solution for use later on.

If you will refer to the electrochemical series of the metals, you will note that silver is near the bottom of the list. Now the chemistry textbook tells us that any metal in this list will displace a metal that lies below it from solution. The most logical metal for us to use would be copper; if we used any metal above copper, copper itself would be displaced along with silver.

Take a copper coin and clean it thoroughly by rubbing with a dilute solution of acetic acid or vinegar. (This experiment is running into money!) Place the clean coin in the

solution in the evaporating dish and let stand for a while.

Mercury is above silver in the electrochemical series and it can also be used to displace silver. This time, use a solution of pure silver nitrate. Add a small globule of mercury and let it stand. Soon you notice crystals of silver "growing" on the mercury.

Now let us go back to our copper coin. By this time sparkling white crystals of silver tinted blue by the solution will have formed. Remove the coin carefully; wash and dry the crystals. If you wish to obtain a coherent mass of silver, you can do so by melting the crystals. Silver melts at 960° . If you have difficulty in reaching this temperature, we suggest you try using a blowpipe. Place a few crystals in a small shallow container, such as a porcelain crucible lid. Grasp the lid with crucible tongs and point the flame from the blowpipe directly upon the crystals. Then blow, brother blow! Create a steady flame, keeping your cheeks inflated. Finally when you are just about ready to give up, the mass will lose shape and a shimmering white liquid of molten silver will form. Pouring this into a large container of water will produce small white balls of pure silver.

Its Compounds

When the Creator assembled this world of ours from some 92 odd substances, He imparted to the compounds of silver a rather unique property — sensitivity to light! For hundreds of years man used metallic silver, never realizing that the compounds of this metal were as valuable as the metal itself. For upon this

seemingly unimportant property the entire photographic industry depends!

You can demonstrate the action of light upon silver compounds in a striking manner. To the second half of the dissolved coin solution prepared earlier, add a solution of sodium chloride. A thick, white precipitate of silver chloride forms. Filter and wash the precipitate thoroughly with water. Next open the filter paper flat and spread the precipitate evenly over it. Lay a hard object, such as a coin, key or nail on the surface of the silver chloride. Now ignite about 2 or 3 inches of magnesium ribbon and hold it directly above the object. After exposure to this brilliant light, the white compound will gradually darken, passing through various shades of pink, red and violet. If the object is now carefully removed, its image will remain as a white design imbedded in violet. Wherever light does not reach, the silver compound remains white.

If sodium hydroxide be added to silver nitrate solution, the brown muddy precipitate of silver oxide is formed. (The hydroxide of silver is not stable.) If this oxide is filtered off and heated, it rapidly decomposes leaving a residue of metallic silver. Silver oxide combined with an organic protein preparation forms the well-known antiseptic, *Argyrol*.

The compounds of silver are varied in color. Add a little silver nitrate solution to solutions of potassium iodide (pale yellow); sodium sulfide (black); potassium chromate (brick-red); sodium phosphate (tan); and potassium ferricyanide (orange).

Silver nitrate is used in medicine as an antiseptic and germicide. Which reminds us of the story of Mrs. Van

Rich. She brought her son to the doctor who advised that he would treat the ailment with nitrate of silver.

"Oh, Doctor," pleaded Mrs. Van Rich, "please use nitrate of gold. Expense is no matter."

2. Gold

➤ PERHAPS no other metal has played such an important part in the destiny of man as has gold. For centuries it has stood as a barometer of wealth and nobility. To secure it, men have fought, suffered and died. Countries have been founded through the search for it; kingdoms have been lost because of it.

Why?

Well, we can supply three reasons. Value. Beauty. Permanence. Obviously, there is a limited supply of the metal available which increases its value. The fact that it is usually found free in nature makes it easy to mine—if you can find it. That it is attractive, we cannot deny. There are very few people who do not appreciate the warm, shining yellow beauty of gold. (We would greatly appreciate having some). And, finally, its appearance is quite permanent. Aluminum becomes dull; iron rusts, copper corrodes, silver tarnishes, but gold remains the same. (Although, it must be dusted occasionally).

The Metal

Despite our glowing words above, metallic gold has very few practical uses. It is really a metal to be looked at, not to be used. About its only use at present is in the manufacture of jewelry. And even then it must be alloyed with other metals, usually copper or silver, as it is too soft to be used in the pure state.

In jewelry, the purity of gold is expressed in carats. A carat indicates the

number of parts of gold in 24 parts of metal. For example, a 14-carat piece would be 14/24 gold and 10/24 other metals. Expressed in percentages, it would be 58-1/3% gold and 41-2/3% other metal. An 18-carat piece would contain 75% gold (18/24). The gold currency formerly used in the United States was 90% gold, or 21.6 carats. And, of course, any 24-carat piece would be solid gold.

Now, how much of this experimenting you can do will depend on how much gold you can secure. Perhaps you can find some bits of discarded gold jewelry around the house—maybe an earring, or a link from a watch band, or a few unused wedding rings.

Gold is relatively inactive and is not attacked by oxygen or ordinary acids. It does, however, react readily with chlorine to form gold (auric) chloride, AuCl_3 . Thus we can dissolve it in aqua regia or chlorine water, both of which supply chlorine.

Prepare aqua regia by mixing together one part of nitric acid with 3 parts of hydrochloric acid. Drop in the gold piece and warm the solution to get the action started. After the metal is dissolved, filter the solution. Your filtrate will most likely be an acid solution of the chlorides of copper and gold. If there was any silver in your metal, it will have been filtered off, as silver is not readily attacked by chlorine and even if it is, the resultant silver chloride is insoluble in water.

To obtain a neutral solution of the mixed chlorides, evaporate the filtrate to dryness and dissolve the solid thus obtained in water. The gold may be separated from this solution by adding a solution of ferrous sulfate, which reduces the gold chloride to metallic gold but does not affect the copper chloride. The reduction is accomplished as follows: $\text{AuCl}_3 + 3\text{FeSO}_4 \rightarrow \text{Au} + \text{Fe}_2(\text{SO}_4)_3 + \text{FeCl}_3$. The precipitated gold is usually brown or black. Filter off the precipitate, scrape into an evaporating dish and heat to obtain the ordinary yellow color. Gold melts at 1063 degrees. If you want to try to melt the finely divided powder into a coherent mass, you might try using a blowpipe.

The Compounds

To obtain a relatively pure solution of gold chloride, dissolve some of the pure metal obtained above in aqua regia. Evaporate to dryness to secure the dark orange-red crystals. Finally, dissolve these crystals in distilled water.

Add a solution of stannous chloride to a dilute solution of auric chloride, just prepared. The "Purple of Cassius" precipitate will be formed. This is a delicate test for gold. So, if any of your friends want to make certain that an item of their jewelry actually contains gold, you can confirm it simply by dissolving the jewelry in aqua regia and applying the above test.

Another test is the orange precipitate formed by adding potassium thiocyanate to gold chloride and gently warming.

If auric chloride crystals are heated gently, aurous chloride, AuCl , is obtained. When this powder is heated

strongly, metallic gold remains and chlorine is evolved.

Oxalic acid will reduce gold chloride solution to metallic gold. The solution must be neutral and the action is hastened by the presence of ammonium oxalate. The metal separates in metallic flakes or will form a golden mirror on the side of the tube: $2\text{AuCl}_3 + 3\text{H}_2\text{C}_2\text{O}_4 \rightarrow 2\text{Au} + 6\text{CO}_2 + 6\text{HCl}$.

When sodium hydroxide solution is added in excess to auric chloride, sodium aurate, NaAuO_2 , is obtained.

Magnesium hydroxide added to auric chloride will form the orange hydroxide, $\text{Au}(\text{OH})_3$. This can be filtered, dried, and carefully heated to 100 degrees to obtain auric oxide, Au_2O_3 , a brown powder. Further heating will give the purple aurous oxide, Au_2O . Still further heating will result in metallic gold and oxygen is evolved.

Rather unusual reactions are obtained with potassium iodide. Add potassium iodide solution to auric chloride in small portions, keeping the *latter* always in excess. A yellow precipitate of aurous iodide, AuI , is formed, soluble in excess of the iodide. But if you reverse the procedure by adding the auric chloride to the potassium iodide and keeping the *iodide* in excess, a dark green solution of potassium-auric-iodide, KIAuI_3 , forms followed by a dark green precipitate of auric iodide, AuI_3 , which is unstable and changes to the yellow aurous iodide.

Well, at this point the experiment is becoming too expensive for us, so we must stop.

At least there is one consolation.

You can save all of your solutions and change all compounds back to metallic gold simply by applying strong

heat. Thus all of the gold you have used can be recovered again. (It says here).

3. Copper

► TO THE BEST of our knowledge, copper was the first metal used by man. Articles made from it have been found which are over 6000 years old. The metal is found in the free state rather widely and its metallurgy is relatively simple. Ores contain copper combined as the oxide, hydroxide, carbonate or sulfide. The latter, which is the most important, must be smelted. The product, usually a mixture of several metallic sulfides, is mixed with coke and roasted again. A blast of air is introduced which oxidizes any iron sulfide present to iron oxide. The latter combines with the silica which had been added to form ferrous silicate and is poured off as slag. Of course when the air is added, cuprous oxide is also formed. This combines with the remainder of the copper sulfide to form free copper: $2 \text{Cu}_2\text{O} + \text{Cu}_2\text{S} \rightarrow 6 \text{Cu} + \text{SO}_2$.

You can obtain copper in the home laboratory by the reduction of copper oxide. Mix together 3 grams of cupric oxide (CuO) with $\frac{1}{2}$ gram of charcoal and place in a crucible or in a hard-glass test tube. Heat strongly for about ten minutes. When cool, examine the residue for traces of metallic copper.

Copper is malleable, ductile and flexible. It is an excellent conductor of electricity.

Chemically it is rather inactive. However if exposed to moist air for any length of time, it will be coated with the familiar green "corrosion".

This is *verdigris*, a basic carbonate of copper $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$. You will find that copper readily dissolves in nitric acid, to form copper nitrate with the evolution of brown fumes of the oxides of nitrogen. If dilute nitric acid is used, nitric oxide is obtained whereas nitrogen dioxide is formed when the concentrated acid is used.

It will react with concentrated sulfuric acid to form cupric sulfate. However, in this case, *sulfur dioxide* is liberated. The copper is oxidized to the cupric ion, and the acid is reduced to sulfur dioxide: $\text{Cu} + 2 \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{SO}_2 + 2 \text{H}_2\text{O}$.

Copper will not react with hydrochloric acid.

As you have probably noted, most soluble salts of copper form a blue solution. Cupric chloride is green in concentrated solution, but will turn blue as the solution is diluted.

When ammonia is added to cupric sulfate solution, an intense blue solution is obtained. This is tetramminocupric sulfate, a typical complex salt of copper.

When hydrogen sulfide is bubbled through a solution of a copper salt, the black sulfide, CuS , is precipitated. This precipitate will dissolve in nitric acid.

Light blue cupric hydroxide, $\text{Cu}(\text{OH})_2$, is precipitated when alkalis are added to copper solutions. It will dissolve in ammonia.

Reddish-brown cupric ferrocyanide

is precipitated by potassium ferrocyanide.

Needless to say, copper is an extremely useful and important metal. It is used in more than a thousand alloys! You are familiar with its use in telephone and telegraph lines, in wires and hundreds of electrical instruments. It is also used in electrotyping, electroplating, etc.

We usually think of copper in the penny, but actually it comprises 75% of our five-cent coins, 10% of our silver coins and 10% of the extinct gold coins. It is in fact, a most important alloying metal. It forms alloys with practically all metals except lead. Brass, bronze, German silver, Britannia metal, gun metal, bell metal and Cupraloy are just a few of the popular alloys of copper.

Prepare a solution of copper sulfate in a beaker and drop in a clean iron nail. You will soon notice that the nail is covered with a coating of copper. Here the iron has gone into solu-

tion (as iron sulfate) and *displaced* the metallic copper.

Clean a copper penny by rubbing it with steel wool and cleanser. Drop it into a solution of silver nitrate. After a short while, the penny will be covered with shining crystals of silver. The solution turns blue as copper sulfate is formed.

If you want a "silver" penny, a better way is to plate it with mercury. Drop a clean shining penny into a solution of mercuric chloride. After twenty minutes, remove the coin. It will be colored black. Rub it briskly with a dry cloth. This will require considerable "elbow grease". But if you rub long enough and hard enough, you will obtain a bright "silver" penny.

When we consider copper as a coin, we think of it as the lowest valued metal. But, truly, in the aspect of industrial usefulness, it is one of the most valuable of metals.

4. Tin

► THE COMMON reference to anything cheap as "tinny," has brought tin a reputation it does not deserve. In fact, tin is not cheap. It is becoming increasingly scarce and hence more expensive. It has been estimated that only 0.00001 per cent of the earth's crust is tin. Tin is very resistant to corrosion and is useful in protecting other metals through plating. It is also used to produce many alloys including solder, pewter, type metal and Rose's metal.

No one knows who first discovered tin. In one form or another it was apparently known to the Ancients.

It is mentioned in the writings of Pliny and Dioscorides and in the Hebrew and Hindu Scriptures. In fact, Pliny even mentioned the use of tin as a coating to prevent corrosion of copper! Our tin plating is evidently not a new idea.

In 1868 a quantity of blocks of tin stored in the custom house in Leningrad mysteriously turned largely into a gray powder. Scientists were puzzled at this strange transformation of tin. Now we know that it is due to the fact that tin exists in three allotropic forms. At ordinary temperatures it is white malleable metal.

Below 18 degrees it exists as a gray metal which is easily crumbled. Thus, articles made of pure tin are likely to disintegrate in cold weather. The third form occurs above 161 degrees and is a white metal, but very brittle.

Since tin has two valence numbers, it forms two series of salts, *stannous* and *stannic*, when it performs as a metal. However, it also acts as a non-metal and produces the compounds known as *stannites* and *stannates*, which are salts of stannous acid and stannic acid.

To note the action of tin on acids, place five test tubes in a row. In the first, place a dilute solution of hydrochloric acid. In the second, dilute sulfuric acid; in the third concentrated sulfuric acid; in the fourth dilute nitric acid and in the fifth concentrated nitric acid. Drop a small piece of tin in each tube. If the action is slow, heat the two tubes gently. Tin reacts slowly with hydrochloric acid to form stannous chloride. If you care to prepare this compound, continue heating occasionally until most of the tin is dissolved. Filter, and evaporate the filtrate to obtain the crystals of stannous chloride. Tin reacts with dilute sulfuric acid to produce stannous sulfate; however, with the concentrated acid it acts as a reducing agent and sulfur dioxide is formed. With dilute nitric acid, stannous nitrate is obtained. With the concentrated nitric acid, the tin is oxidized and the insoluble meta-stannic acid precipitates.

Dissolve a small quantity of stannous chloride in water. The solution will probably be cloudy due to the insoluble basic salt which is formed. A few drops of hydrochloric acid

should clarify the solution. Add a few drops of sodium hydroxide solution to the stannous chloride. Stannous hydroxide is precipitated. When this precipitate is heated it is dehydrated and the oxide, SnO_2 , is finally obtained. Thus, stannous hydroxide cannot be obtained in the dry state. Add more sodium hydroxide until the precipitate originally formed is redissolved. You now have a solution of sodium stannite, NaSnO_2 . To another portion of stannous chloride, add a few drops of sodium sulfide solution. A brown precipitate of stannous sulfide is obtained. Stannous sulfide will dissolve in ammonium polysulfide solution to produce ammonium thiostannate.

Stannous chloride is a reducing agent. Add a solution of stannous chloride to a solution of mercuric chloride. The mercuric ion is reduced to mercurous and a white precipitate of mercurous chloride is obtained. Similarly, ferric chloride is reduced to ferrous.

Stannic chloride is an unusual compound in that it is liquid at ordinary temperatures and in the pure state does not conduct the electric current, both contrary to the accepted nature of salts. It is prepared by the action of chlorine on tin. In the home lab, it can be prepared in small quantity by dissolving tin in nitro-hydrochloric acid. Carefully mix together three parts concentrated hydrochloric acid with one part concentrated nitric acid. Add a small piece of tin. Chlorine is released by the solution and acts on the tin. After action ceases, add a few drops of sodium sulfide solution. A yellow precipitate of stannic sulfide is obtained.

Tin forms two oxides, stannous, SnO , and stannic, SnO_2 . The former is prepared by carefully heating stannous oxalate. It is a black or greenish-black powder. Stannous oxalate can be prepared by adding oxalic acid to a neutral solution of stannous chloride. Stannic oxide is prepared by heating stannous oxide strongly. It is a white powder when cold and yellow when hot.

The metal itself can be obtained by heating the oxide, SnO_2 , with carbon. If you would like to try this, we suggest you use a blowpipe. Mix the oxide with carbon and place in a charcoal block. Heat in the reducing (inner) flame of the blowpipe. Since tin is rather far down in the list of metals, it can be displaced from solution by more active metals. Simply drop a piece of clean zinc, iron, or aluminum in a strong solution of stannous chloride and allow to stand for a few days. Scrape off the deposit and dry. Look for the tiny crystals of pure tin.

The action of potassium iodide on tin salts is rather interesting. Add a small quantity of potassium iodide to a concentrated solution of stannous chloride. A yellow precipitate is formed at first but continues to redissolve as long as the stannous chloride is in excess. When the potassium iodide is in excess, a thick dark orange

precipitate is obtained. If more stannous chloride is then added, the yellow precipitate is again obtained.

Tin reacts directly with sulfur to produce stannic sulfide. This can be demonstrated in an experiment sometimes called the "mosaic gold" experiment. Thoroughly mix together equal parts of powdered tin and sulfur. Add about $\frac{1}{8}$ th as much ammonium chloride and place the mixture in a crucible. Cover the surface of the mixture with a sprinkling of ammonium chloride, cover the crucible, and heat strongly for about ten minutes. The stannic sulfide will be deposited in beautiful yellow spangles on the crucible lid.

If you have been patient and have tried the foregoing reactions and have been unsuccessful, please do not blame the innocent publishers! It may be all the fault of your stannous chloride! If you have had the compound for a while, no doubt a greater part of it has developed into the basic oxychloride salt, which is insoluble in water. Sometimes, as explained above, a few drops of hydrochloric acid may clarify the solution. But if more acid must be added it will interfere with the reactions described. So, we suggest that you avail yourself of a *fresh* supply of C.P. stannous chloride before you attempt to perform the experiments.

5. Lead

➤ NOW WE HAVE a heavy subject to discuss: lead.

Lead was probably known during the prehistoric age. References to it are found in the Old Testament.

The Babylonians used it for en-

graving and later the Romans used it for water pipes and coins.

Although not plentiful, lead is widely distributed in nature. It occurs chiefly as the sulfide, PbS , known as *galena*. This ore is roasted to obtain

the monoxide, PbO , which is in turn roasted with carbon to obtain the metal.

The low melting point and chemical inactivity of lead make it useful for many purposes. You are familiar with it as waste pipe for plumbing fixtures. It is used in constructing apparatus for the manufacture and handling of sulfuric acid. And, of course, it is mighty important in the manufacture of storage batteries. Also, it is used in many important alloys, such as solder, type metal, pewter, Babbitt metal, and shot.

Metallic Lead

Cut a piece of lead and note that the surface is brightly lustrous at first. However it is soon covered with a dull gray coating containing the monoxide, basic carbonate and lead particles.

You can prepare lead in the laboratory by the reduction of the oxide, PbO , with carbon. Mix together one portion of lead monoxide with two portions of powdered charcoal. Place in a crucible, cover, and heat strongly for about 15 minutes. Allow to cool, and dump the powder out. If you examine it closely, you will find small balls of pure lead. If you wish, you can collect the balls and fuse them into one solid piece.

Lead Monoxide

Heat a piece of lead in a shallow metal pan or evaporating dish. It melts at 327.5 degrees. The molten metal is soon covered with a light yellow scum. This is lead monoxide, PbO . It can also be obtained by carefully heating lead nitrate crystals.

Lead monoxide is a yellow powder known as *massicot* and commercially

as *litharge*. When mixed with glycerine it forms a quick-hardening cement used by plumbers. It is also used in lead glass, varnishes, for glazing pottery and as a pigment for rubber.

Red Lead

If you will heat lead monoxide strongly (to 500 degrees) in the air, it will gradually turn red in color as red lead oxide, Pb_3O_4 , is formed. Actually red lead is not an oxide itself, but a mixture of two lead oxides, PbO and PbO_2 . If you want to be technical about it, it could be called *plumbous plumbate*, Pb_2PbO_4 .

It is used as a rust-protective paint for iron or steel, in cements, varnishes, matches, etc.

Lead Dioxide

Add a small quantity of red lead to dilute nitric acid in a test tube. Immediately a brown precipitate of lead dioxide is obtained.

It is a vigorous oxidizing agent and is used as such in the manufacture of dyes. It is also used as electrodes in batteries, in rubber substitutes and with amorphous phosphorus as the ignition surface for safety matches.

White Lead

White lead has been widely used for years in paints. It is the basic carbonate, $\text{Pb}(\text{OH})_2 \cdot 2 \text{PbCO}_3$.

Add a solution of sodium carbonate to a solution of lead nitrate to obtain the snow-white precipitate. Now add a few drops of sodium sulfide, or bubble hydrogen sulfide gas through the mixture. The white precipitate turns black, which indicates that white lead paint should not be used where it will be exposed to sulfide vapors.

Lead Chloride

Lead chloride is soluble in hot water but not in cold. Prepare a dilute solution of lead nitrate in a test tube and add a few drops of hydrochloric acid. The heavy white precipitate of lead chloride is formed and settles quickly to the bottom of the tube. Heat the solution to boiling and continue to boil until the compound is entirely dissolved. If necessary, add more water. Then place the tube in a container of cold water. Soon you will see the lead chloride crystallize in sparkling flakes which will fall rapidly through the solution, not unlike a miniature snowstorm.

Other Compounds

When you add a solution of potassium dichromate to a solution of lead nitrate, a bright yellow precipitate is formed. This compound, lead chromate, is known as *chrome yellow* and is used as a yellow paint pigment.

Lead iodide is also bright yellow in

color. Prepare it by adding potassium iodide solution to the lead nitrate.

Lead monoxide dissolves in acetic acid to form lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. This compound is also known as *sugar of lead*. It is used in various ointments, in dyeing and printing cottons.

When sodium hydroxide is added to lead nitrate, lead hydroxide, $\text{Pb}(\text{OH})_2$, is obtained. If this hydroxide is dissolved in acids, *plumbous* salts such as plumbous chloride, PbCl_2 , are formed. If it is dissolved in bases, *plumbites*, such as sodium plumbite, Na_2PbO_2 , are formed.

When lead dioxide is dissolved in concentrated sodium hydroxide, sodium *plumbate*, Na_2PbO_3 , is obtained.

Lead tetraethyl, $\text{Pb}(\text{C}_2\text{H}_5)_4$, used for "ethyl" gasoline, is made by treating sodium and lead alloy with ethyl bromide.

As lead salts are poisonous, be sure to wash your hands thoroughly after experimenting.

6. Aluminum

History

► I SUPPOSE that many doubts could have entered his mind.

"Why should I attempt it when so many have failed?"

"How can I afford the necessary equipment?"

"Who would be interested if I were successful?"

"What use would there be for the product?"

But, fortunately, none of these doubts overshadowed the burning desire of Charles Martin Hall to find a practical way to obtain aluminum from its ore.

We, who take aluminum for granted, find it hard to visualize that less than a generation ago the metal was virtually unknown except as an expensive laboratory curiosity to scientists. And, the irony of it all was that aluminum is the most abundant metal on earth! No one had yet found a successful method to obtain it as a free metal in any worthwhile quantity. Like the tale of the Ancient Mariner, it was a "water, water everywhere and not a drop to drink" situation. This was the situation that Charles Hall sought to correct. With home-made batteries in his home-built

laboratory in the woodshed, plus a large amount of will and determination, Hall discovered the electrolytic method of extracting aluminum from bauxite which is still in use today.

But the story of aluminum goes back still further. It all began in 1759 when the German chemist Andreas Marggraf proved that alumina was a distinct compound . . . different from magnesia and lime. This certainly did not seem like an epoch-making discovery, but nevertheless it was the starting link in the long chain of events which brought us aluminum which we find so useful today.

Although Marggraf suspected that alumina contained a new element hitherto unknown, he was unable to isolate it. Sir Humphry Davy became interested in the compound also and he attempted to decompose it with his voltaic pile which he had used previously to isolate sodium, potassium, and the alkali earth metals. But the stubborn alumina would not respond. Berzelius, too, attempted to isolate the metal and was unsuccessful.

It remained for the Danish chemist Oersted to prepare aluminum for the first time in history. Suppose we let him describe the method he used in his own words:

"Rapidly heated with potassium amalgam, it (aluminum chloride), is decomposed, potassium chloride and aluminum amalgam being formed. This amalgam is very quickly decomposed in contact with the atmosphere. By distillation without contact with the atmosphere, it forms a lump of

metal which in color and luster somewhat resembles tin."

Such was the birth of aluminum. This was a difficult and dangerous experiment. Wöhler later repeated the experiment but could not obtain the metal. He did, however, finally succeed in preparing it by a method of his own which consisted of heating anhydrous aluminum chloride with metallic potassium. This was indeed a violent reaction and the platinum crucible he used became white hot!

The French chemist Deville improved upon Wöhler's method and made large-scale production possible, but the price was prohibitive.

And so we come to Charles Martin Hall in the United States who finally solved the problem when he conceived a cheap method to obtain the evasive element. Gradually, through the years the price of aluminum has dropped from \$150 to a few pennies per pound. Certainly we need not elaborate on the role aluminum plays in our economy today. It has become one of the most important and highly useful metals known.

Physical Properties

Aluminum has three important physical properties: lightness, strength, and durability. The pure metal is silvery white but quickly becomes covered with a thin coat of oxide which gives it the familiar dull appearance. This layer of oxide is a blessing, as it prevents further oxidation and is responsible for the durability of the metal.

As it is listed high in the electrochemical series, aluminum is quite active. Place a small piece of the clean metal in a solution of dilute hydrochloric acid. Note the rapid action as

the metal dissolves. Sulfuric acid also attacks the metal, but less vigorously. Strangely enough, aluminum does not dissolve in nitric acid; hence this acid may be shipped in aluminum containers and tank cars. Prepare a concentrated solution of sodium hydroxide and drop a clean piece of aluminum in it. Note the reaction. This illustrates why acids and alkalies should not be heated in aluminum saucepans.

Aluminum melts at 600 degrees. You can probably melt it in the home lab by heating it in a Bunsen burner flame. Or, you can use a blowpipe with an alcohol lamp flame. Place the metal in a porcelain crucible lid. Grasp the lid with tongs and direct the blowpipe flame onto the metal.

Aluminum burns with a brilliant white flame. Sift a *small* quantity of aluminum powder into an alcohol lamp flame. It will burn in blinding white flashes of light. Be sure to use small quantities here and guard against fire.

Chemical Properties

Aluminum is a powerful reducing agent and can be used to reduce the oxides of certain other metals. This reduction is known as the "Goldschmidt Process," named after its founder. To demonstrate the reaction, mix together equal quantities of powdered aluminum and iron oxide. Use *small quantities!* Place the mixture in a large dry fireclay crucible. Place the crucible in a bed of sand, or, preferably, outside. Drop a piece of burning magnesium ribbon into the crucible. Keep your face away! A violent reaction takes place as the aluminum combines with the oxygen in the

oxide leaving the iron free. The heat is usually sufficient to melt the iron and the reaction is used in welding ("thermit" process). After the crucible is thoroughly cool, dump the contents out and examine with a magnet for small particles of iron. If the mixture in the crucible fails to ignite with the magnesium ribbon, you can add an "ignition mixture." Mix together equal quantities of powdered magnesium and barium peroxide. Carefully pour this mixture on top of the iron oxide and aluminum mixture. When you drop the burning magnesium strip into the crucible, it will ignite the ignition mixture which will in turn ignite the basic mixture.

Compounds

► THE COMPOUNDS of aluminum have been in use many years before the metal itself. Although today the metal is more popular than its compounds, the latter still play an important part in our daily lives.

Since aluminum sulfate is the most easily obtainable aluminum salt, we will use it as our starting point. Prepare a solution of aluminum sulfate by dissolving two or three grams of the compound in 50 cc. of water. (The strength of the solution is not important for these reactions). To a portion of the aluminum sulfate solution, add 5 or 10 cc. of ammonium hydroxide. A white, voluminous precipitate of aluminum hydroxide is obtained. This is one of those two-faced compounds which plague chemistry students by acting both as a base, $\text{Al}(\text{OH})_3$, and as an acid, H_3AlO_3 . Thus, when dissolved in acids, aluminum hydroxide forms aluminum compounds. Add dilute hydrochloric acid to the aluminum

hydroxide precipitate. Stir until the precipitate is entirely dissolved. This reaction will be accompanied by dense fumes due to the formation of ammonium chloride as a side reaction with any unreacted ammonium hydroxide. You now have a solution of aluminum chloride, AlCl_3 .

Add a small portion of sodium hydroxide to aluminum sulfate solution. Note that the white precipitate is formed as before. Now continue to add sodium hydroxide solution until the precipitate is entirely dissolved. Here the aluminum hydroxide performs as an acid and we obtain a solution of sodium aluminate, NaAlO_2 . If you care to prepare the compound, simply evaporate the solution to dryness. Sodium aluminate will dissolve readily in water to form a solution which is strongly alkaline. It is used in industry for dyeing and printing fabrics, sizing paper, as a water softener, and in the manufacture of soap.

Fill two test tubes half full with aluminum sulfate solution. Add a few crystals of cobalt nitrate to one solution to color it pink. Add a few crystals of nickel sulfate to the other solution to color it light green. Now add a small portion of ammonium hydroxide to each container. Note that the aluminum hydroxide obtained is not pure white, as before, but instead pink and green respectively. This property to carry a color or impurity along with it makes aluminum hydroxide quite useful in many applications. For example, in the dye industry the color of a dye is attached firmly to the cloth by the absorbent power of aluminum hydroxide. This property is also utilized in the purification of water, in which case alum-

inum hydroxide is precipitated and upon settling removes much suspended matter and even many bacteria. Sizing paper is another example. Here the process brings to paper the ability to carry ink . . . which adheres to the aluminum hydroxide.

Versatile Oxide

Aluminum oxide is a most fascinating compound because it occurs in so many different forms. It can be prepared as a soft, white powder. Or it can assume the form of hard gritty powder. The soft type dissolves in acids; the hard type does not. It occurs in nature as the mineral, *bauxite*, one of the most important sources of the metal. It occurs also as the extremely hard and crystalline *corundum* and *emery* which form the most popular abrasives. It is prepared artificially as *alundum*, also used as an abrasive and as a refractory. But, the most romantic form of all is the transparent crystal variety in which form it is known as the *ruby* and the *sapphire*. These gems are now prepared synthetically by fusing powdered alumina in an oxyhydrogen flame and crystallizing. If you are interested in performing this experiment at home, add a little chromium trioxide to produce the ruby and a little iron oxide and titanium dioxide for the blue sapphire. Or, if you prefer an oriental amethyst, this color is due to the presence of manganese. Even "star" gems (those exhibiting asterism) can be made by careful treatment of the materials. Thus the manufacture of synthetic gems has become an extensive industry and it is becoming increasingly difficult to distinguish an artificial gem from a

natural one. (Although the experts can still tell!).

To prepare aluminum oxide, first prepare a solution of the hydroxide by mixing together solutions of aluminum sulfate and ammonium hydroxide. Filter off the precipitate. Carefully scrape it from the filter paper into an evaporating dish. Heat gently until all water is driven off. This is the soft type of aluminum oxide. More intense heating will produce a compound similar to bauxite and still more intense heat will produce the hard "corundum" type.

When a soluble sulfide (such as sodium or ammonium) is added to aluminum sulfate, the hydroxide, not the sulfide, is precipitated. Aluminum sulfide exists only in the dry state. Whenever water is added, it immediately hydrolyzes: $\text{Al}_2\text{S}_3 + 6\text{HOH} \rightarrow 2\text{Al}(\text{OH})_3 + 3\text{H}_2\text{S}$. Thus to prepare aluminum sulfide it is necessary to heat the two elements together.

This property of hydrolysis occurs also with aluminum carbonate and acetate. When either of these compounds are added to water, aluminum hydroxide is precipitated. Again, the reaction is put to good use. For

example, cloth which is soaked in a solution of aluminum acetate becomes saturated with the aluminum hydroxide produced by hydrolysis. The hydroxide fills all the spaces between the threads and renders the cloth waterproof.

The popular "alum" is made by mixing together equal molecular quantities of potassium sulfate and aluminum sulfate and dissolving in water. Upon evaporation, crystals of alum are formed.

Pure clay is a double oxide of aluminum and silicon, $\text{Al}_2\text{O}_3 (\text{SiO})_2 \cdot 2\text{H}_2\text{O}$, is white in color, and is called *kaolin*. This substance is used to make porcelain and china.

Aluminum sulfate is obtained from clay by treating it with sulfuric acid. Perhaps you would like to try this. Simply digest the clay in sulfuric acid for several hours. Filter off the residue and test the filtrate for the presence of aluminum. A good test is to add sodium hydroxide which will form the hydroxide at first but will redissolve in excess alkali. Ammonium hydroxide will produce the hydroxide, but it will not redissolve in excess.

7. Magnesium

► DURING THE eighteenth century, a strange white powder appeared in Italy and was widely sold as a "cure-all". The compound, known as *magnesia alba*, was quite popular and consequently its composition and source were kept secret. Naturally, the insatiable curiosity of the scientist would not allow this condition to exist for long, and the chemist Friedrich Hoffmann soon prepared the pow-

der from the mother liquors of common salt. We doubt very much that he knew he was experimenting with a new element.

It remained for the illustrious Sir Humphrey Davy to obtain the first magnesium in the metallic state. He isolated a very small quantity of it during the series of his famous electrochemical experiments performed in 1808 — the same year in which he

isolated barium, strontium, calcium, and boron. (Sodium and potassium were isolated the year before). It was not until 1831 that magnesium was obtained in any sizeable quantity by Bussy, a French chemist. He prepared the metal by heating magnesium chloride with metallic potassium — a difficult and dangerous experiment to perform even today.

As with many of the elements, magnesium was then forgotten until recent years. Now its popularity is increasing rapidly. An interesting proof of this is that the production of magnesium in 1944 in the United States was 100 times more than that produced in 1939!

Magnesium is stronger and lighter than aluminum. It forms many useful alloys which are resistant to wear and corrosion, easily machined, resonant, light, strong, and good conductors of heat.

In powder or thin strip form magnesium burns with a brilliant white light which is rich in short wave lengths. Thus it is the principal ingredient in flashlight powders for photography.

Holding it in tongs or pliers, ignite a 2-inch strip of magnesium metal. Do not stare directly into the blinding light. Note the white ash remaining. Burn a few strips and collect the ash in a mortar. Grind to a powder. This is chiefly magnesium oxide, MgO , along with the nitride, Mg_3N_2 . The oxide mixed with water forms the hydroxide, $Mg(OH)_2$. A suspension of the hydroxide in water is sold as the familiar anti-acid laxative, "milk of magnesia". It is best prepared in the laboratory by adding an alkali (such as sodium hydroxide) to

a solution of a soluble magnesium salt (such as magnesium chloride or sulfate). Or, to put it another way, mix lye with Epsom salts and obtain milk of magnesia!

Flashlight powder consists of powdered magnesium with an oxidizing agent. Carefully mix together 4 parts of finely powdered potassium nitrate with one part of magnesium powder. Place in a metal pan and sprinkle a little sulfur on top of it. Ignite the mixture with touch paper. A blinding white fire results. Remember the four rules which must always be observed when experimenting with pyrotechnics:

- (1) *Mix immediately before using.*
- (2) *Use only small quantities.*
- (3) *Keep your face away.*
- (4) *Ignite in a place where sparks will not reach flammable objects, preferably outdoors.*

The touch paper which is used as a fuse may be prepared by soaking strips of filter paper in concentrated potassium nitrate solution and then drying.

Magnesium is quite active and will dissolve in most acids (except hydrofluoric). Place in four test tubes dilute solutions of acetic, hydrochloric, nitric, and sulfuric acids. Drop a small strip of clean magnesium into each solution. Note how rapidly it dissolves. You now have solutions of magnesium acetate, chloride, nitrate and sulfate. The latter is the well-known "Epsom salts". Magnesium sulfate was first separated from mineral waters at Epsom, England over 200 years ago and has been known by the name Epsom salts ever since. If you want to prepare it, continue to add magnesium to the sulfuric acid until no

more dissolves. Dilute with water, filter, and evaporate almost to dryness. Then let stand in a warm place until the crystals form. Of course this is an expensive and impractical way of preparing Epsom salts; it is not prepared this way commercially. You have now prepared Epsom salts from magnesium metal. Our next project for you is to take the Epsom salts and convert it back to the metal!

It may surprise you to know that magnesium will also dissolve in ordinary baking soda. To demonstrate, prepare a concentrated solution of baking soda and drop a small strip of clean magnesium into it. Note the bubbles that begin to form as the metal gradually disintegrates. It is similarly affected by ammonium chloride solution.

Magnesium is located high in the Electromotive Series and will displace many metals from solution. Drop a piece of clean magnesium in silver nitrate solution. Soon the magnesium is completely dissolved and in its place will remain sparkling crystals of pure silver. You can try displacing other metals from their solutions such as zinc, nickel, iron, copper, mercury, tin, lead, etc.

The uses of magnesium and its compounds are manifold. The alloys are used extensively in airplanes, automobiles, and boats; also, in sewing machines, typewriters and conveyor

equipment, light-weight ladders, and many other types of engines, machinery, and tools. Both milk of magnesia and Epsom salts, already discussed, are used in medicine. The oxide is also used in tooth powders and toilet powders. Mixed with magnesium chloride it forms a strong cement known as magnesia cement, Sorel's cement, or zylolith. It is further used as a heat insulator in the form of porous fire brick or as a plaster. When CO_2 is passed into milk of magnesia a compound with the formula $4\text{Mg} \cdot \text{CO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ is obtained. This compound mixed with asbestos is known as *85 per cent magnesia*, widely used as an insulation for boilers and pipe lines. The mineral calcium-magnesium metasilicate is known as *asbestos*. The mineral known as *soapstone* is hydrated magnesium silicate. In pulverized form it is known as *talc* and is the main component of talcum powders. The highly efficient drying agent, *anhydron*, is anhydrous magnesium perchlorate. Many more uses of this versatile metal and its compounds can be listed, but we must stop some time.

The newest source of magnesium compounds is from the sea which represents a practically inexhaustible supply. Magnesium chloride is extracted from the water. The compound is fused and the metal obtained by electrolysis.

8. Nickel

➤ ONCE UPON A TIME, the American five cent piece was worth five cents. With a nickel one could buy a candy bar, cigar, ice cream cone, soft drink and even a hot dog or loaf of bread.

But now the nickel is only part payment on these items and about the only thing it can be used for is in the church collection plate.

But the monetary value of the coin

does not interest us (much), for we are concerned with what it is made of rather than its worth. Strangely enough, there is very little nickel in a nickel. Actually, it is 25% nickel and 75% copper. Having nothing better to do, suppose we see if we can determine the presence of the two metals in a nickel.

First, obtain the nickel. During the war years, nickel was so badly needed that its use in coinage was curtailed and silver was used instead. So try and obtain a nickel dated prior to 1941 or after 1947. We don't want our nickel coins adulterated with silver.

Clean the coin thoroughly with steel wool and cleanser. Then drop it into a dilute solution of nitric acid. If necessary, apply heat and add additional acid from time to time until the nickel is entirely dissolved; then, filter. We now have a solution of copper and nickel nitrates.

How shall we separate the two compounds? Both nitrates are soluble in water and alcohol. Both hydroxides are greenish-blue and both are soluble in acids and ammonium hydroxide. Both oxides are black and soluble in acids. Both sulfates, chlorides and acetates are soluble, whereas both sulfides, carbonates and oxalates are insoluble.

Before we proceed further, suppose we transfer our compounds to the chlorides. First add a solution of sodium hydroxide to the mixed nitrates forming a precipitate of nickel and copper hydroxides. Filter off, then add more sodium hydroxide to the filtrate and re-filter. Combine the two precipitates and dissolve the mass in dilute hydrochloric acid. We now

have a solution of copper and nickel chlorides. Thinking of copper chloride brings to mind the fact that *cuprous* chloride is insoluble in water! Of course, our solution contains *cupric* chloride. Why not add a reducing agent to precipitate the copper as cuprous chloride? You can, if you wish. Add a solution of stannous chloride and filter off the precipitate. You will then have a solution of nickel chloride — but, mixed with tin!

So, let's plan another attack. We find there is one difference in the two sulfides. Copper sulfide is precipitated by hydrogen sulfide in the presence of acid, whereas nickel sulfide is not! Take your solution of the two chlorides and add a little more hydrochloric acid just to make certain that the acid will be in excess. Next, bubble a stream of hydrogen sulfide gas into the solution. (The hydrogen sulfide is generated by the action of dilute HCl on iron sulfide). Or, if you prefer, add a solution of sodium sulfide. Copper sulfide will be obtained as a black precipitate. Filter it off and again add sulfide to the filtrate. No doubt additional copper sulfide will be precipitated. Filter the second time and combine the precipitates. Save the filtrate, which should be nickel chloride.

Of course we do not want copper in the form of the sulfide. So let's get it back to the chloride again. This is done by dissolving the sulfide in concentrated hydrochloric acid. It will dissolve with difficulty and you will have to coax it along, using heat if necessary. Dissolve as much as you can; then filter.

Now we have a solution of copper

chloride and a solution of nickel chloride (we hope). Pour some of the copper chloride in a watch glass and drop a clean nail in the solution. It will soon be covered with pure copper, displaced by the more active iron.

You can easily verify the presence of nickel in your nickel chloride solution by adding a few drops of dimethylglyoxime solution. This famous "nickel-testing" reagent forms a scarlet red precipitate even in very dilute solutions of nickel.

Now if you feel ambitious, you can actually obtain the metal. Add sod-

ium hydroxide to a portion of your nickel chloride solution. Filter off the nickel hydroxide, dry, and heat strongly to obtain black nickel oxide. Transfer this to a charcoal block and heat strongly in the reducing portion of a blowpipe flame. Examine the residue carefully for minute traces of metal. If it is nickel, it will be attracted by a magnet.

Well, this experiment has cost you at least one good nickel. We hope that you have received five cents worth of enjoyment from it.

9. Mercury

► MERCURY is one of the most fascinating of the elements. The fact that it is liquid at ordinary temperatures results in rather unusual properties for a metal. To the beginner in chemistry, mercury is ever a source of wonder and amusement.

Mercury is certainly no stranger to the chemist. It was known to the ancient Chinese and to the Egyptians as far back as 1600 B.C. The metal is found free in small quantities, but more abundantly as the sulfide in the mineral *cinnabar*, HgS . It is isolated with relative ease by roasting the ore. Italy and Spain produce the most mercury; however, it is also found in the United States and Mexico. It "freezes" at -39 degrees and boils at 357.25 degrees.

Amalgams

Mercury forms alloys with other metals which are known as *amalgams*. The amalgams of tin, silver, and gold are used for filling teeth. Sodium amalgam is an active reducing agent.

You can prepare it by grinding the elements together in a mortar. Be sure the mortar is thoroughly dry. Use a drop of mercury no larger than a pea. Cut a still smaller piece of sodium metal into tiny pellets and add to the mercury. Carefully grind the metals together. The resultant sodium amalgam is decomposed by water, forming sodium hydroxide and hydrogen.

If a small quantity of sodium amalgam is added to a concentrated solution of ammonium chloride, slightly warmed, ammonium amalgam is formed but decomposes rapidly. The amalgam swells up and forms a porous mass which quickly disappears.

Compounds

Mercury forms many colorful compounds which are no less interesting than the metal itself. Mercuric chloride (corrosive sublimate) is one of the most important compounds. It is used to prepare other mercury compounds, also for disinfecting, preserving wood,

tanning leather, electroplating, embalming, etching steel and mordanting fur. It is *very poisonous*! It precipitates protein in the cells of the body, usually in the cells of the kidneys. The fatal dose is 0.2 to 0.4 gram. We suggest that you exercise *extreme caution* when experimenting with this compound.

Prepare a moderately strong solution of mercuric chloride by dissolving 2 grams in 20 cc. of water in a beaker, heating if necessary. Cool, and add 5 cc. of the solution to an equal quantity of sodium hydroxide solution. A yellow precipitate forms. This is not the hydroxide, but the *oxide*, HgO . The hydroxide decomposes immediately even at ordinary temperatures. Transfer the liquid to a hard-glass Pyrex test tube and allow the precipitate to settle; then carefully pour off the liquid on top. Apply gentle heat to the test tube until all moisture is driven off. The yellow color will change to orange-red. Now apply strong heat. The oxide will decompose. Oxygen is given off and the mercury sublimes in tiny droplets along the upper wall of the test tube. You can scrape these droplets together by careful manipulation with a glass rod to form a globule of mercury.

Sulfides

Prepare a source of hydrogen sulfide by adding dilute hydrochloric acid to ferrous sulfide in a test tube. Attach a cork and delivery tube. Allow the hydrogen sulfide to bubble through 5 cc. of mercuric chloride solution in another test tube. A heavy white precipitate forms which rapidly turns yellow, brown, and finally black. This is amorphous mercuric sulfide, HgS . The same compound can be

prepared by grinding the elements together in a mortar. The red crystalline variety, cinnabar, is formed by sublimation.

Iodides

Prepare a solution of potassium iodide and add a small quantity of mercuric chloride solution. A yellow solution of mercuric iodide forms at first which rapidly dissolves to form the double iodide, K_2HgI_4 . Continue to add mercuric chloride until the yellow precipitate forms again. It will rapidly change to red. Upon heating it turns yellow and back to red again on cooling. Filter off and carefully dry the precipitate. Transfer to an evaporating dish and heat gently. The powder will turn yellow and remain so on cooling. Now poke the compound with a glass rod. It will turn red wherever it is touched. Heat mercuric iodide in an evaporating dish and cover with a glass plate. The vapors of the compound will condense on the glass in the form of black crystals. These will also turn red when touched. Sometimes, however, this experiment unaccountably fails. Mercuric iodide can also be formed by the direct union of the elements.

Mercurous nitrate is the only readily soluble mercurous salt. Dissolve a small quantity in a test tube of water. If the solution is cloudy (due to the formation of the insoluble $\text{Hg}_2(\text{OH})\text{NO}_3$) add a drop or two of nitric acid.

Calomel

Add a little dilute hydrochloric acid to mercurous nitrate solution. The white curdy precipitate is mercurous chloride, commonly known as

calomel. It is used in medicine as a cathartic and diuretic.

When sodium hydroxide is added to mercurous nitrate solution, a dark brown precipitate forms which has been assumed to be mercurous oxide, Hg_2O . However, recent accurate examination has shown the precipitate is actually a mixture of mercury and mercuric oxide.

You can make a "silver" penny by

plating it with mercury. Allow a clean sparkling penny to stand in a solution of mercuric chloride for several hours. Remove and dry. The coin will be black. Rub briskly with a soft cloth. The black color will disappear and a silvery lustre will be obtained.

Remember, all mercury compounds are poisonous. Wash your hands thoroughly after experimenting.

10. Selenium

► **SELENIUM** can be purchased at most chemical supply houses. It is priced about the same as magnesium, and using only small quantities will not make the cost prohibitive. One ounce should be sufficient for the experiments mentioned here.

Like sulfur, selenium exists in several allotropic forms.

Metallic: This is the form in which selenium is usually supplied commercially, either as lustrous, metal-like sticks or as a dark gray powder. Although termed "metallic," it must be remembered that selenium is a non-metal (sulfur family).

If you can obtain selenium as a powder, sift a small quantity of it into an open flame. It burns brilliantly with a bright blue flame forming the dioxide which, true to the sulfur family tradition, has a disagreeable odor, resembling rotten radishes, of all things!

You can melt the powdered selenium into a coherent metal-like mass by placing it in a porcelain evaporating dish and heating. This form of selenium is insoluble in carbon disulfide.

Vitreous: If you melt selenium in

an evaporating dish and quickly pour the molten mass into a beaker of cold water, a brittle, dark brown or black mass will be obtained. This is still selenium though in another form, and still insoluble in carbon disulfide.

Amorphous: This is a dark red powder so different from the metallic variety that it is hard to believe it is the same substance. We will prepare it later on. Incidentally, it is soluble in carbon disulfide.

Colloidal: Obtained as a dark red powder. It dissolves in water forming a red fluorescent solution.

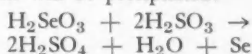
Crystalline: Dark red, brown or black crystalline powder.

Selenium Dioxide, SeO_2

Unlike sulfur, the oxide of selenium is not a gas but a solid. Usually it is obtained in the form of a white crystalline powder. Dilute about 2 cc. of nitric acid with an equal quantity of water. Add a small amount of selenium and heat until it is entirely dissolved. The selenium is oxidized by the nitric acid forming a solution of selenous acid, H_2SeO_3 . To obtain the dioxide, evaporate the solution to

dryness. The powder remaining has the typical selenium-odor of radishes.

Now prepare selenous acid again by dissolving a portion of the SeO_2 in hot water. If sulfurous acid be added to this solution, the red variety of selenium will be precipitated:



The precipitate formed is at first yellow, then it gradually darkens through various shades of orange to brick red. The sulfurous acid for this reaction may be prepared by adding sodium sulfite or bisulfite to a dilute solution of hydrochloric acid.

Hydrogen sulfide will precipitate both sulfur and selenium from selenous acid. Dissolve another portion of the solid dioxide in water. You can either bubble hydrogen sulfide through this solution or add a solution of sodium sulfide and avoid the disagreeable odor of H_2S . The yellow precipitate formed will turn red upon heating.

Hydrogen Selenide, H_2Se

Hydrogen forms with selenium a colorless gas with an odor of rotten horseradish. It is more toxic than H_2S , and must not be inhaled. It is prepared by adding dilute hydrochloric acid to ferrous selenide. The ferrous selenide is formed by heating together equal quantities of iron filings and powdered selenium.

Lead the H_2Se into a solution of sodium sulfite, and a mixture of sulfur and selenium is precipitated. Sel-

enides are formed by leading the gas into solutions of salts of the metals. Try preparing the selenides of lead, silver, copper, nickel, etc. Hydrogen selenide will burn when ignited and will dissolve in water, similar to H_2S .

Other Compounds

No trioxide of selenium is known. Selenic acid, H_2SeO_4 , white, hygroscopic crystals, will dissolve in water forming a corrosive, acid liquid. It is formed in solution by oxidizing silver selenite with bromine.

Selenium oxychloride, SeOCl_2 , is a very active and corrosive liquid attacking many metals.

Uses of Selenium

The metallic variety of selenium has a very unusual property. It is a fair conductor of electricity; however, this conductivity is greatly increased by light. Perhaps you can set up some arrangement in the home lab to demonstrate this property. This peculiar characteristic of selenium is utilized in photoelectric cells and photometers.

Added to glass in minute quantities, selenium imparts a ruby color, familiar in the taillight lenses of automobiles. It is also used, similarly to sulfur, in vulcanizing rubber.

Selenium is obtained as a by-product during the refining of copper. It is not produced in any quantity because the demand for it is small. Perhaps some day one will find a greater use for it.

11. Tungsten

► THE BRIGHT GLOW of tungsten in the electric light bulb is familiar to

all. But less familiar are the many other important roles that this valu-

able metal plays in industry; for it acts unseen behind the scenes without pomp or glory. It forms extremely hard alloys which practically revolutionized the tool industry. They are used in making axles of automobiles and steel rails. Other alloys are valuable in electronic devices such as anticathodes of X-ray tubes, filaments for radio tubes, contact points, etc.

Let us examine this important "lesser known" element in more detail.

History

The existence of a new substance in certain Swedish minerals was suggested by Scheele as early as 1781. The same substance was discovered in the mineral *wolfram* by two Spanish chemists, the de Elhuyar brothers. In 1783 they succeeded in isolating the new metal by heating the substance (tungstic acid) with carbon.

Thus tungsten made its quiet appearance and then lay practically forgotten for almost a century before it was put to important use.

Isolation

The reduction of tungsten trioxide, WO_3 , is not easily accomplished in the home laboratory. Carbon or hydrogen could be used, but both require extremely high temperatures. Perhaps better results can be obtained by using metallic sodium as the reducing agent.

First, we must obtain the oxide. The most common compound of tungsten is sodium tungstate and we will use it as our starting point. Dissolve 3 grams of it in 15 cc. of water. Add to this a solution of 5 cc. hydrochloric acid in 5 cc. of water. A white precipitate of tungstic acid forms

which rapidly turns yellow. Filter, and transfer the precipitate to an evaporating dish. Heat gently until all water is driven off. Grind the remaining solid to a fine powder in a mortar. Finally, heat again strongly for about 10 or 15 minutes. The powder will turn dark orange but will regain its yellow color in cooling. This is tungsten trioxide, WO_3 .

Caution

Sodium is a powerful reducing agent and sometimes dangerous; therefore proceed cautiously. Place a *small* quantity of thoroughly dry tungsten trioxide in a thoroughly dry porcelain crucible. Cut a small piece of metallic sodium — *no larger than a pea*. Clean it, cut into several smaller pieces, and drop into the crucible with the tungsten trioxide. Immediately cover the mixture with a layer of common salt, about $\frac{1}{4}$ inch thick. Place a loose fitting cover on the crucible and apply moderate heat. The action should proceed quietly, but it is best to place the apparatus in a place where no danger will occur from flying sparks in the event the sodium becomes a bit obstreperous. Heat for about 15 minutes; then let the crucible cool thoroughly before removing the cover. When cool, carefully shake out the layer of salt. The bottom of the crucible will be covered with a black, brittle powder which, if your experiment was successful, is tungsten. If all the sodium has not reacted it will be necessary to heat again under the layer of salt. Of course you are familiar with the explosive reaction of sodium and water; it will not be necessary to caution you against the careless use of the latter in extracting the metal or wash-

ing the crucible. As the tungsten requires a temperature of 3370 degrees to melt it, we will have to be content to leave it in powdered form.

Identification

The "blue oxides of tungsten" present a characteristic test for the presence of that element. Add a little hydrochloric acid to a solution of sodium tungstate and drop in a small piece of zinc. The precipitate formed is first white, then yellow, and finally passes through various shades of blue. The latter color is formed by the reducing action of the hydrogen bubbling through the solution. If potassium ferrocyanide be added to the acid solution instead of the zinc a greenish orange-yellow color is obtained. Stannous chloride gives a white precipitate.

We have found that the easiest way to obtain tungsten is to break an electric light bulb. If you can obtain such a bulb, it will be interesting to verify the composition of the filament. We refer to that portion of coiled, brittle, white wire suspended

from wire supports in the center of the bulb.

Our first difficulty is to bring the tungsten into solution. It is scarcely attacked by acids, even by aqua regia. The powdered metal will dissolve in boiling KOH solution, but the solid metal, as in the filament, will not. Our only alternative, then, is fusion with alkali. Place one or two grams of solid sodium hydroxide in an evaporating dish. Add a small piece of the filament-wire and heat until the solid melts and most of the metal is dissolved. Sodium tungstate is formed. When cool, dissolve in water. Make acid with HCl and add a piece of zinc. The blue color betrays the presence of tungsten.

But suppose you have followed instructions and no blue color is obtained? When you added water to the fused alkali, was a white precipitate formed at first which dissolved when more water was added? If so, in all probability you have a solution of sodium tantalate and your filament was not tungsten, but tantalum.

12. Titanium

" . . . as I did in the case of uranium, I shall borrow the name for this metallic substance from mythology, and in particular from the Titans, the first sons of the earth. I therefore call this new metallic genus TITANIUM."

Martin Heinrich Klaproth, 1795

► TITANIUM is another one of those elements usually classified as "rare," but in reality it is quite plentiful. Actually, titanium is tenth in the list of

more abundant elements. Strange as it may seem, titanium is more plentiful than either carbon or chlorine! Despite its abundance, it is still unfamiliar to most people mainly because its usefulness, so far, has been limited. Nevertheless, it does have some interesting properties, so let us become better acquainted.

History

Titanium was discovered in 1791 by an English clergyman, The Rev. William McGregor. Mr. McGregor

suspected the existence of a new substance in the minerals obtained from his own parish. Although he announced his discovery, he did not investigate further and the new element was soon forgotten.

Klaproth resurrected the element four years later and it was he who named it titanium.

Titanium is not found in the elemental state and it is very difficult to isolate. Klaproth, Rose, Vauquelin, Wollaston, and others all tried to isolate the metal without success. Berzelius obtained a black powder by reducing potassium fluotitanate with potassium, but whether the powder contained much titanium is open to question. Similarly, in 1849 Wöhler and Deville obtained a gray metallic powder which they thought was titanium, but others claimed the powder was a nitride of titanium.

Finally in 1887, the metal was obtained 95% pure by Nilson and Pettersson. They reduced titanium tetrachloride with sodium in an air-tight cylinder. Moissan also prepared it in his electric furnace.

M. A. Hunter prepared the purest metal (99.9%) in 1910 by heating pure titanous chloride with sodium in a machine steel bomb.

The Metal

Although we have been referring to titanium as a metal, it is actually one of those "in-between" elements acting as a metal in some of its compounds and as a non-metal in others. It is brittle, silvery-white in appearance or in the amorphous state is a dark gray powder. It melts at 1800 degrees C.

As described above, its isolation is not accomplished very easily, there-

fore we suggest you purchase the metal itself from a chemical supply house. Limited production keeps the price high, but you will need only a small quantity for these experiments.

Titanium burns with unusual brilliance forming the dioxide and the nitride. You can demonstrate this by sifting a small quantity of powdered titanium into an open flame. Do not use too much, as it burns rapidly with a blinding white light.

Its Compounds

Titanium dissolves in dilute acids forming titanous salts.

Dissolve a few pieces of the metal in dilute hydrochloric or sulfuric acid, heating if necessary. When as much as possible has dissolved, filter the solution and evaporate to dryness over a gentle heat.

Titanous chloride (titanium trichloride), $TiCl_3$, consists of dark violet deliquescent crystals soluble in water to form a lovely red-violet solution. Titanous sulfate (titanium sesquisulfate, $Ti_2(SO_4)_3$), is a green crystalline powder insoluble in water but soluble in dilute HCl or H_2SO_4 giving a violet colored solution. These salts of titanium act as vigorous reducing agents. Evidence of this fact can be shown by adding titanous chloride solution to a solution of silver nitrate; the latter is reduced to metallic silver which forms as a gray precipitate.

If you want to be sure that your solution contains titanium, add a small quantity of hydrogen peroxide. A yellow color indicates the presence of titanium. A yellow color is also formed with oxalic acid.

Dissolve a few pieces of titanium in

aqua regia (3 parts HCl and one part HNO_3). Heat gently to start the reaction; it will then proceed of itself with vigor. Filter the resultant solution and evaporate nearly to dryness. Then add 20 or 30 cc. of water and to this solution add a little ammonium hydroxide. A white precipitate of titanous hydroxide (titanic acid) forms. To obtain the dioxide, TiO_2 filter and heat the precipitate to dryness. Apply only gentle heat as the compound will turn yellow if strongly heated. Titanium dioxide is an excellent white pigment used in paints.

Titanium Tetrachloride

Titanium tetrachloride, TiCl_4 , is an interesting compound. It absorbs moisture from the air and evolves dense white fumes. With ammonia it is used to produce smoke screens. It is formed by passing chlorine over a heated mixture of titanium dioxide and carbon. Place a small quantity of manganese dioxide and dilute HCl in a test tube. Attach a stopper and de-

livery tube. Lead the delivery tube to the bottom of another test tube which contains a mixture of TiO_2 and charcoal. Apply heat under both tubes. Allow the chlorine to pass over for about 10 or 15 minutes. Then disconnect the apparatus and add a small quantity of cold water to the TiO_2 -charcoal mixture. Next pour in a little ammonia and observe the smoke screen.

Future

Here is an element available in plenty, but which has not yet been fully put to work. It is gradually becoming more useful and perhaps some day someone will find easier methods of producing it and other ways of using it. Perhaps at some future date titanium will be as familiar to everyone as aluminum is today. For we must remember that not so long ago aluminum itself was one of those "rare" abundant elements, difficult to isolate, and for which no use could be found!

13. Antimony

► ANTIMONY has been known since 3000 B.C. Indeed, according to ancient historical lore, the Oriental women used the metal to beautify their eyebrows. And we thought the use of cosmetics was a modern trend!

No one knows who discovered antimony, but the first investigation of its properties is accredited to Basil Valentine, who wrote a book on the subject entitled, "The Triumphal Chariot of Antimony."

The Metal

Antimony is found chiefly as the mineral *stibnite*, which is a trisulfide,

Sb_2S_3 . The metal is silvery-white with a brilliant luster. It is more readily available commercially in the form of powder, and we shall use this as our starting point.

The metal melts at 630° , and you will be able to reach this temperature easily with a blowpipe. Place a small quantity of the black, powdered antimony in a small hole in a charcoal block. Direct the blowpipe flame on the metal, blowing with inflated cheeks to insure a steady flame. Pour the melted globule on a sheet of white paper. It will break up into several miniature balls which will roll over

the paper in various directions, each forming a track of charred paper behind it. Also, you can observe the silvery appearance of the solid metal in contrast to the black powder.

The Trioxide, Sb_2O_3

Antimony powder will burn in air or oxygen with a bright light to form the trioxide. Sift a small quantity of the powder into a flame to observe this reaction.

This oxide is also obtained by the action of nitric acid on the metal. Add a small portion of the powdered metal to dilute nitric acid and heat gently. Soon a miniature "snowstorm" is formed consisting of particles of antimony trioxide.

Antimony is one of those annoying elements that we call *amphoteric*, meaning that its hydroxide acts either as a base, $\text{Sb}(\text{OH})_3$, forming salts such as sodium meta-antimonite, NaSbO_2 ; or as an acid, H_3SbO_3 forming compounds such as antimony trichloride, SbCl_3 . There are several elements which act this way just to make life confusing for chemistry students.

Sodium Meta-Antimonite, NaSbO_2

Filter off the precipitated trioxide and dissolve a small portion of it in sodium hydroxide solution, heating if necessary. The resulting solution is sodium meta-antimonite. It is strongly hydrolyzed and reacts with water to form a solution of sodium hydroxide and antimonous acid.

Antimony Trichloride, SbCl_3

By dissolving the trioxide in hydrochloric acid, the trichloride is formed. This substance forms large, soft crys-

als and is sometimes known as "butter of antimony." It is also hydrolyzed and reacts with water to form the insoluble antimony oxychloride, SbOCl .

Antimony Pentachloride, SbCl_5

The pentachloride is formed in a fascinating reaction involving the direct union of the elements. Prepare a tall cylinder of chlorine gas. Chlorine gas may be generated by heating dilute hydrochloric acid with manganese dioxide in a flask to which is attached a one-hole stopper and delivery tube. Allow the gas to flow through the delivery tube into an empty cylinder. When the cylinder is filled, as you can observe, cover with a glass plate and disconnect the generator. Now, remove the plate and sift finely powdered antimony into the cylinder of chlorine. As each particle falls it will burn with a flash of light.

Antimony Trisulfide, Sb_2S_3

This substance is found in nature as a black powder, but can be precipitated in the laboratory as an orange-red powder. To prepare the black sulfide, simply heat together equal portions of powdered antimony and sulfur. When all reaction has ceased, remove the mass and powder in a mortar. To form the beautiful orange-red variety, dissolve a small portion of the black sulfide in dilute hydrochloric acid. This forms antimony trichloride, as prepared previously. Now bubble hydrogen sulfide into the solution. Gradually the orange-red precipitate appears. (The hydrogen sulfide can be generated by adding dilute hydrochloric acid to iron sulfide).

Antimony Pentasulfide, Sb_2S_5

When antimony trisulfide is dis-

solved in yellow ammonium sulfide, the pentasulfide is formed upon the addition of acid. Technically, for those who are interested, the soluble ammonium thioantimonate is first obtained. Upon addition of acid, thioantimonic acid is formed which rapidly decomposes and antimony penta-

sulfide is thrown down as an orange precipitate.

Tartar Emetic

This well-known compound is obtained by heating antimony trioxide with potassium bitartrate. It is a basic salt, $K(SbO)C_4H_4O_6$, used in medicine as an emetic and expectorant.

14. Arsenic

➤ THE CHIEF fame of arsenic arises from its use in murders and committing suicide. It is rapidly being replaced for the latter by sleeping tablets, and even in murders, the cyanides are bringing strong competition. In general, we do not recommend arsenic for suicide as it is slow, agonizing, and usually fatal.

The Metal

Arsenic has been known for centuries. As an ore, it was mined by the Romans and Greeks. But it was not isolated as a metal until many years later.

The "arsenic" known to the general public actually is the trioxide of arsenic, As_2O_3 . In fact, probably few people realize that arsenic exists as a metal. But, of course, we know better.

Seriously, arsenic *is* a deadly poison and must be handled carefully. Use only small quantities; do not inhale any vapors. Wash your hands and all containers thoroughly immediately after experimenting.

Arsenic is easily reduced from the trioxide by carbon. Mix together equal quantities of arsenic trioxide and powdered wood charcoal. Place a *small* portion of this mixture in a

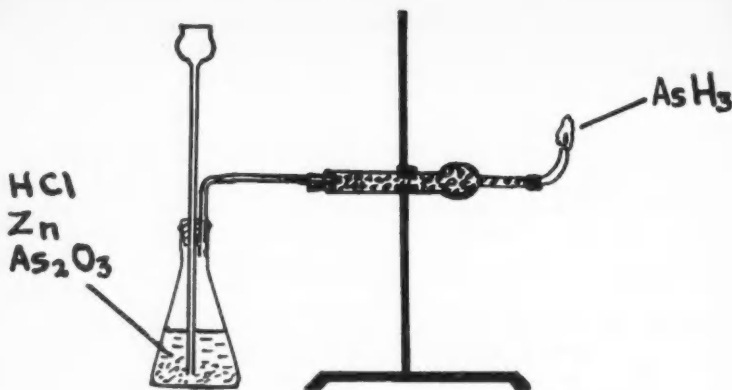
large, narrow, dry test tube. Heat gently at first, gradually increasing. The arsenic will be released as a vapor and condense in the cooler part of the tube, forming a metallic deposit on the walls. If enough heat is applied, you may observe the yellow vapor. Don't inhale! When cool, carefully break the tube and scrape off the metallic crystals with a glass rod.

Arsenic burns in the air forming the trioxide. Sift a small quantity of powdered arsenic into a flame. Note the flash of light and the white cloud of smoke, which consists of fine particles of As_2O_3 . Note also the garlic-like odor characteristic of arsenic. Perform this in a well-ventilated room.

Pure arsenic metal is not soluble in hydrochloric or sulfuric acid. Nitric acid, however, oxidizes it to arsenic acid, H_3AsO_4 . Arsenious acid, H_3AsO_3 , is formed by dissolving the trioxide in water.

Colorful Compounds

Prepare a solution of arsenious acid by dissolving a small portion of arsenic trioxide in water. It will be necessary to heat, as the oxide is not very soluble in cold water. Add a little ammonium hydroxide, then pour in a solution of copper sulfate. The



➤ PREPARATION of Arsine.

beautiful yellow-green precipitate, which will dissolve in excess ammonia, is known as *Scheele's Green*.

To arsenious acid solution, add ammonium sulfide. Arsenious sulfide, As₂S₃, is formed in colloidal suspension. If a few drops of hydrochloric acid be added, it will separate as a bright yellow precipitate, known as *orpiment*.

Temperamental Crystals

Here is an unusual experiment, if it works. To a solution of 5 cc. hydrochloric acid in 5 cc. of water, add ½ gram of arsenic trioxide. Boil the mixture for a few minutes in a small flask. Allow to cool slowly. Shake the flask gently from time to time. Eventually crystals will form, each one accompanied by a flash of light. You had better not plan this experiment for a demonstration show, because sometimes for some unexplainable reason, it just doesn't work.

Reinsch's Test

When a solution of arsenic is boiled

with hydrochloric acid and a piece of copper is added, a gray film of arsenic will be deposited on the copper. This serves as a test for arsenic and if only a trace be present it will appear on the copper. To demonstrate, boil a little arsenic trioxide (or any other arsenic compound) with a dilute solution of hydrochloric acid. Immerse in the solution a bright, clean strip of copper. The gray film will betray the arsenic.

Arsine—Marsh's Test

As nitrogen combines with hydrogen to form ammonia, NH₃, so arsenic combines with hydrogen to form *arsine*, AsH₃. Arsine is exceedingly poisonous and there is also some danger of explosion in its preparation. Therefore, we do not recommend this experiment for the inexperienced worker.

Set up a hydrogen generator with a calcium chloride tube attached for drying the gas. Fill the tube with granular calcium chloride, and attach

a glass jet to the end of it, as shown in the accompanying diagram.

Generate hydrogen by pouring dilute hydrochloric acid on zinc metal in the flask. Allow the action to continue for a *full five minutes*. Then *cautiously* ignite the gas at the glass jet. As an added precaution wrap a towel loosely around the generator to prevent flying glass in the event of an explosion. Never take chances with hydrogen! Now while the gas is burning, pour a *small* amount of arsenious acid (or any arsenic compound) through the thistle tube into the generator flask. Note the change in color of the flame and also the garlic-like odor. (Do not breathe it.) Let the flame touch the inside of a porcelain evaporating dish. The presence of

arsenic is indicated by the metallic deposit on the cool porcelain. This is an extremely delicate test by which, it is claimed, 0.00001 g. of arsenic can be detected.

Uses

Arsenic seems to be most useful in the role of a killer. As stated before, the oxide is used in murder and suicide. The metal is used to harden lead in manufacturing lead shot. The compounds are used in insecticides for killing the boll weevil and other destructive insects. It is used in rat poisons. It is even used to kill weeds. But, like many other poisons, it can also be used to heal. *Salvarsan*, an organic-arsenic compound, is invaluable in the treatment of the dreaded syphilis.

15. Bismuth

➤ BISMUTH is one of those quiet and unassuming elements about which we hear little. It does not have any spectacular properties or exciting history. It rarely makes the headlines and performs its duties without fanfare.

The metal is used chiefly as a component of low-melting alloys which are important in automatic sprinkling systems for fire control. The compounds of bismuth are used in pharmaceutical preparations for upset stomach and ulcers and in patent medicines such as "Pepto-Bismal." Certain compounds have also been used in the treatment of syphilis.

Bismuth has been known for centuries, but the early alchemists confused it with lead and tin, probably because of its low melting point. It was not until 1737 that the French

chemist Hellot recognized bismuth as an individual metal. His findings were confirmed by Geoffroy in 1753 who described the metal and its properties.

Bismuth is not plentiful. It is found most abundantly as the free element in the United States, Canada, Mexico, Peru and Spain. A smaller portion is found in the form of the oxide, $\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$, *bismite*, and of the sulfide, Bi_2S_3 , *bismuthenite*.

The metal is reddish-white with a bright metallic luster. It is hard and brittle. It melts at 269 degrees, which is lower than lead but higher than tin. The molten metal expands on cooling.

You can melt bismuth quite easily by placing a few small pieces in a spoon and heating over a Bunsen

burner flame. At a bright red heat (if you can get it that hot) the metal will burn with a bluish flame and the oxide, Bi_2O_3 , is obtained.

Compounds

Bismuth dissolves slowly in hot concentrated hydrochloric acid and sulfuric acid, but quite readily in nitric acid. Therefore, we will prepare bismuth nitrate as our starting point. Dissolve several small pieces of bismuth in 25 cc. of dilute nitric acid. The resultant light yellow-colored solution is bismuth nitrate, $\text{Bi}(\text{NO}_3)_3$. Bismuth salts hydrolyze readily forming basic salts known as "sub" compounds. Pour 5 cc. of the bismuth nitrate just prepared into 20 cc. of water. A miniature "snow-storm" of white crystals is formed which rapidly settles to the bottom of the vessel. This is bismuth *sub*nitrate, which is insoluble in water. It has been used for years in the preparation of face powders. There is a possibility that it can form nitric acid by hydrolysis with perspiration; therefore, it is not the best choice for this use. It appears that rubbing the face with nitric acid is not to be recommended.

Add 5 cc. of your bismuth nitrate solution to 10 cc. of dilute sodium hydroxide solution. The heavy white precipitate is bismuth hydroxide, $\text{Bi}(\text{OH})_3$. Filter it off and scrape into a dry evaporating dish. Heat gently at first and gradually increase the heat until the white powder turns to a brownish-red color. It will pass through various shades of yellow before reaching this state. When you cease heating, the brownish-red powder will again turn yellow. This is bismuth trioxide, Bi_2O_3 .

Add another 5 cc. portion of bis-

mutn nitrate to a solution of potassium chromate. The bright orange-yellow chromate of bismuth is formed.

Bismuth iodide behaves rather strangely. Prepare it by adding 5 cc. of bismuth nitrate solution to an equal quantity of dilute potassium iodide solution. A dark brown precipitate results. Now add an additional quantity of moderately concentrated potassium iodide solution. The precipitate dissolves to form a clear golden orange liquid. This liquid is known as "Dragendorff's Reagent" and is used as a test to determine the presence of alkaloids. Now if you will pour this clear liquid into a beaker of water, it will precipitate out again.

Other compounds may be prepared if you desire. For example, the trioxide, as obtained above, may be dissolved in hydrochloric acid to obtain bismuth chloride or in sulfuric acid to obtain the sulfate. If water is added to the solutions, the basic salts (subchloride and subsulfate) are formed. The subchloride decomposes immediately to form the oxychloride, BiOCl . This compound is known as "pearl white" and is used as a pigment.

When bismuth is fused with sulfur, the sulfide, Bi_2S_3 , is obtained. This compound is not soluble in yellow ammonium sulfide, which affords a method of separating it from compounds of arsenic and antimony. If bismuth trioxide is fused with potassium hydroxide, the brown potassium bismuthate, KBiO_3 , is formed. This compound is hydrolyzed by water precipitating bismuth pentoxide, Bi_2O_5 .

Bismuth will displace silver from its salts. Drop a piece of bismuth in a solution of silver nitrate. You will

soon observe the crystals of silver "growing" on the bismuth.

Thus we have bismuth—useful in the control of fire and indigestion!

16. Sodium

► WE ARE SO familiar with the properties of metals like iron, copper and aluminum that when we consider sodium it is hard to conceive that it is a metal. Yet, in a chemical sense, sodium is more metallic than iron, copper or aluminum. When freshly cut it has the appearance of silver. It is soft and light in weight, melts at 97.7° . It is extremely active and tarnishes rapidly on exposure to air. Hence it must be kept immersed in a liquid which contains no oxygen, such as kerosene or naphtha.

You can well imagine that such an active metal would never be found free in nature. The compounds of sodium were known for centuries before the metal was ever obtained. Chemists were familiar with sodium hydroxide but they did not know its composition. Some thought it was an element, others thought it was a compound of nitrogen. All efforts to decompose it had failed. Then the new science of electro-chemistry came into being. Sir Humphry Davy, one of the foremost experimenters in this field, first tried to decompose aqueous solutions of the caustic alkalis. He succeeded in decomposing the water but not the alkali. Next he tried to decompose fused potassium hydroxide with his battery. In this he was successful and was the first person ever to isolate the metal potassium. A few days later he tried the same experiment with sodium hydroxide to isolate sodium.

The discovery of sodium and potassium aroused the public interest in a dramatic manner—probably much in the same way that the sulfa drugs and penicillin have done in our time. Practically every chemist was interested and attempted to prepare the wonder metal in his own laboratory. The famous chemists Gay-Lussac and Thenard prepared the alkali metals without electricity by reducing the hydroxide with metallic iron at a high temperature. Another famous chemist, Friedrich Wöhler, also isolated potassium without an electric current by heating potash and charcoal to white heat in a graphite crucible.

You can purchase sodium metal from a chemical supply house. It is not expensive, and one ounce will be plenty for these experiments. Be sure the metal is kept under oil, kerosene or naphtha at all times. Do not handle it with your bare hands.

Cut a piece of sodium the size of a pea. Note the shiny luster as you cut it. Press the metal gently between blotters to remove excess oil, then drop it into a large pan of water (such as a cake pan). It will zig-zag rapidly in all directions over the surface of the water until it is dissolved. Keep your face away. Often after the sodium has apparently all dissolved, there is a final loud "pop" as the last particle explodes. Wait for this "pop" before you get too close. The water in the pan is now sodium hydroxide, as you

can prove by adding a few drops of phenolphthalein solution. Or, for a little novelty to the above experiment, add the phenolphthalein first, then drop in the metal. As it dissolves, the water turns pink.

Now place clean water in the pan, moisten a piece of filter paper and allow it to float on the water. Drop a *small* piece of sodium metal on the paper. The metal will ignite with a bright yellow flame. This floating flame provides an unusual effect. Again, wait for the final "pop" before approaching the pan.

Sodium is a powerful reducing agent. Cut a few very small pieces of the metal, dry carefully, and mix with one gram of copper oxide in a porcelain crucible. Place a lid on the crucible and heat gently. The action may be somewhat violent, so use caution. After all action ceases, remove the lid and see if you can find any pieces of metallic copper. We obtained several metallic balls the size of a pin head by this method.

Sodium combines directly with many elements. For example you can prepare synthetic salt. Place a dry, freshly-cut piece of sodium in a dry

deflagration spoon and lower into a jar of chlorine gas. Allow it to remain in the jar for about thirty minutes. Upon examination, you will notice the formation of a white powder, which is common salt. (Better not taste it!) The reaction is simply a direct union of two elements:

$$2 \text{Na} + \text{Cl}_2 \rightarrow 2 \text{NaCl}.$$

Sodium unites with mercury to form the *amalgam*. Place a small drop of mercury in a mortar. Cut a still smaller piece of clean dry sodium into very small particles. Add to the mercury and press the two elements together with the pestle. You will hear miniature explosions as the amalgam is formed. As with the metal itself, sodium amalgam is decomposed by water with the evolution of hydrogen.

Sodium melts easily as can be demonstrated by heating a small piece in a porcelain dish. It will burn in air with its characteristic yellow flame.

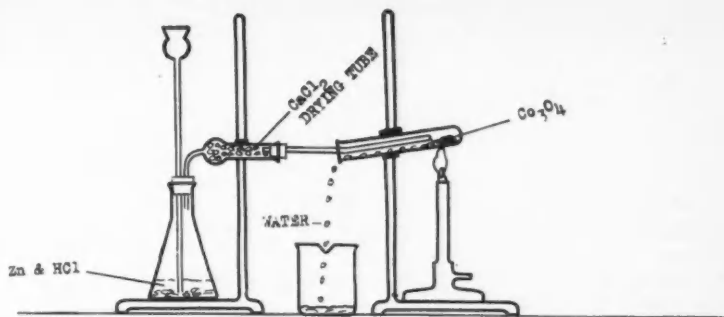
Sodium metal is quite useful in the preparation of many sodium compounds, such as the peroxide, azide, etc. It is used to produce the important tetraethyl lead, in various organic reactions and in sodium lamps and photoelectric cells.

17. Cobalt

► ALTHOUGH ISOLATED first in 1735, it has been only recently that cobalt has found wide use in industrial alloys. It forms alloys with chromium which are highly resistant to acid corrosion. It is an important component of the many high-speed steels on the market today. As you know, cobalt is magnetic but it also has the unusual property of adding magnetic strength to alloys containing it. One example is

the new alloy, *Alnico*, which is capable of lifting over fifty times its own weight! You amateur radio experimenters will be familiar with the Alnico magnets used in high-fidelity loudspeakers. Alnico consists of aluminum, nickel and cobalt. You will note its name comprises the chemical symbols for these three elements.

The most common compound of cobalt is cobaltous chloride, CoCl_2 .



➤ REDUCTION of cobalt from the oxide by means of hydrogen.

$6\text{H}_2\text{O}$, so we will use it as our starting point.

Place a few crystals of cobaltous chloride in a dry evaporating dish and heat gently. Note that the red crystals turn deep blue. Allow to cool and add water, a few drops at a time. As water is added, the blue crystals form a blue solution which rapidly turns red. This illustrates an important property of cobaltous chloride—when dehydrated it is blue—with water it is pink. We can utilize this property to prepare a "sympathetic ink." Write on a piece of paper with a pen dipped in a solution of cobalt chloride. The writing is invisible. To make it appear, heat the paper gently. When the paper is exposed to moist air, the writing disappears again. This same principle is used in toy barometers. A cloth or paper is soaked with concentrated cobalt chloride solution and allowed to dry. When the air is dry it appears bluish (fair weather), but in moist air it turns pink (rainy weather).

Now prepare a moderately concentrated solution of cobaltous chloride. Add a solution of sodium hydroxide.

The blue precipitate formed at first rapidly turns pink. This is cobaltous hydroxide, $\text{Co}(\text{OH})_2$. (If the precipitate does not turn pink, heat gently until it does). Filter it off and scrape onto a dry evaporating dish. Apply rather strong heat. The powder turns black as the oxide, Co_3O_4 , is formed. This oxide is known as cobaltous oxide, or cobalto-cobaltic oxide.

The metal itself is a bit difficult to isolate in the home laboratory. However you may obtain it in a finely divided state by reduction of the oxide with hydrogen. Set up an apparatus as shown in the accompanying diagram. The finely powdered oxide (as prepared above) is placed in the test tube. Hydrogen is generated in the flask by adding dilute hydrochloric acid to zinc. Allow the gas to flow over the oxide in the test tube for three or four minutes. Then start to heat the tube as shown. Use extreme caution as is always necessary when working with hydrogen. Use a Pyrex hard glass test tube. Keep all flames away from the mouth of the tube. Do not apply any flame until you are

pretty sure all of the air in the tube has been displaced by the hydrogen.

Pure cobalt is a silvery-grey malleable metal which is magnetic. It tarnishes very slowly in air. It reacts slowly with dilute hydrochloric and sulfuric acids. However, it dissolves rapidly in nitric acid.

Cobalt forms many complex compounds, several of which can be used as tests for the metal. For example, if ammonium sulfocyanide is added to a concentrated cobalt solution, a double

salt $(\text{Co}(\text{CNS})_2 \cdot 2\text{NH}_4\text{CNS})$ is formed. This salt can be dissolved in a mixture of amyl alcohol and ether to obtain a beautiful blue solution.

The yellow potassium cobalt nitrite, $\text{K}_3\text{Co}(\text{NO}_2)_6$, is precipitated when a mixture of potassium nitrite and dilute acetic acid is added to a cobalt solution. In this reaction, nitrous acid is liberated which oxidizes the cobalt salt.

Dimethylglyoxime will produce a brown coloration.

18. The Rare Earth Elements

► WE SHALL never cease to marvel at the amazing systematic pattern into which all of the elements fall. If one arranges the elements in the order of their increasing atomic numbers, it will be noticed that after each group of eight elements similar chemical and physical properties reappear. These elements with the similar properties may then be grouped to form chemical "families." We proceed quite nicely down the list of elements until we strike element No. 57. Then another amazing point is observed. Following element 57 the next 14 elements, through No. 71, are remarkably similar to *each other*. They do not fall into any of the family groups we have listed. In short, they break up our systematic pattern.

These are the so-called "rare earth" elements. They just do not seem to belong anywhere. What shall we do with them? What is the rhyme or reason for their existence? Usually in Periodic Tables they are listed separately outside the regular table or in a special group at the bottom.

Because the properties of these mysterious fifteen elements are so nearly identical it is extremely difficult to separate them. Even today, a number of them have not yet been prepared in a pure state. Very few uses have been found for the elements and consequently they lay neglected for years. The famous chemist Sir William Crookes once said: "The rare earths perplex us in our researches, baffle us in our speculations, and haunt us in our very dreams. They stretch like an unknown sea before us, mocking, mystifying and murmuring strange revelations and possibilities."

The most plentiful and most popular of the rare earths is cerium. As it is readily obtainable, we shall experiment with it as a representative of the group. The oxalate is the most common of its compounds. You should be able to secure cerium oxalate from any chemical supply house, or maybe even the local druggist will sell you a small quantity. The compound you obtain will be marked "N.F." and will contain varying amounts of the

The Rare Earth Elements

Name	Symbol	Atomic Number	Atomic Weight	Melting Point	Year Discovered
Lanthanum	La	57	138.92	860	1839
Cerium	Ce	58	140.13	800	1803
Praseodymium	Pr	59	140.92	950	1885
Neodymium	Nd	60	144.27	850	1885
Promethium	Pm	61			1945*
Samarium	Sm	62	150.43	1350	1879
Europium	Eu	63	152.0	1150	1889
Gadolinium	Gd	64	156.9		1880
Terbium	Tb	65	159.2		1843
Dysprosium	Dy	66	162.46		1886
Holmium	Ho	67	163.5		1878
Erbium	Er	68	167.2	1250	1843
Thulium	Tm	69	169.4		1878
Ytterbium	Yb	70	173.04	1800 (?)	1878
Lutetium	Lu	71	175.0		1906

* Prepared synthetically by atomic bombardment.

oxalates of lanthanum, praseodymium, neodymium, and minute traces of other rare earth elements. We certainly shall not attempt any purification or any separation of the other elements at this time.

Cerous oxalate is a light pink powder used in medicine as a gastric sedative. It is insoluble in water.

Cerium dioxide, CeO_2 , is formed by heating the oxalate. Place one gram of cerous oxalate in a dry evaporating dish. Heat strongly until a heavy brown powder is obtained. Pure cerium dioxide is pale yellow. The brown color here is due to the oxides of lanthanum, praseodymium, etc. Cerium dioxide is used as a contrast medium in roentgen-ray work.

Cerous Chloride, CeCl_3 , is colorless and very soluble in water. Dissolve as much of the cerium dioxide just prepared as possible in 10 cc. of dilute

hydrochloric acid, heating if necessary. Filter.

Cerous Hydroxide, $\text{Ce}(\text{OH})_3$, is obtained as a white precipitate by adding a solution of sodium hydroxide to the filtered solution of cerous chloride.

Cerous Nitrate, $\text{Ce}(\text{NO}_3)_3$, is used in medicine in the treatment of chronic diarrhea, dyspepsia and pyrosis. Its solution in the proportion of 1:1000 checks the growth of bacteria. To prepare it, filter off the hydroxide just prepared and dissolve it in dilute nitric acid.

Ceric Nitrate, $\text{Ce}(\text{NO}_3)_4$, is a yellow compound. Ceric salts are less stable than cerous. Generally they can be obtained by oxidation of the cerous salts. Add a small amount of nitric acid to your solution of cerous nitrate along with lead dioxide (PbO_2). Heat the solution and keep adding lead dioxide until no more dissolves. Boil for

five or ten minutes. Then filter to obtain the yellow-colored solution of ceric nitrate.

A delicate test for cerium can be formed by adding hydrogen peroxide to a soluble cerium salt followed by ammonium hydroxide. A light brown precipitate is formed. Try this test on your cerous chloride solution.

Cerium metal is extremely difficult to isolate in the pure state. It is found in *monazite sand* along with other rare earths. The mixed chlorides of the various rare earths are prepared from this mineral and then by electrolysis in the fused state, an alloy of rare earth metals is obtained. This alloy is known as *misch metal*. It is *pyrophoric*, meaning it emits sparks when scratched. Alloyed with iron it is used in cigarette lighter 'flints.'

Dissolve a few flints in dilute hydrochloric acid and filter. You, of course, can easily determine the presence of the iron in this alloy by adding a few drops of the solution to potassium ferrocyanide solution. The

familiar light blue precipitate is formed (Turnbull's blue).

Now, how to separate the iron from the cerium? Well, we notice one peculiarity of cerium. Cerium oxalate is soluble in *hot* ammonium oxalate solution, while ferrous oxalate is not. So add a solution of ammonium oxalate to your solution of ferrous-cerous chloride. Now heat the solution almost to boiling and filter quickly while still hot. Now if our theory is correct, the cerium oxalate will pass through while the ferrous oxalate will remain on the filter paper. To prove the theory, test the filtrate for cerium as described above.

Despite much laborious research work, the properties of the rare earths still are not fully known. Because some of them are formed as by-products of atomic research a new interest has been created. Here is a field which invites investigation—for surely some good use can be found for these "haunting, mysterious" elements.

19. Alloys

► THE DICTIONARY describes an alloy as "a substance composed of two or more metals fused together." This seems to be a logical explanation, so we will accept it.

With the exception of aluminum and copper, most metals are not used in the pure state. For scientists have found that by mixing metals together they can form many "new" metals, some with properties entirely different from the component metals. In this way soft metals can be hardened, brittle metals made tough, corrosion eliminated, melting points lowered or raised, etc.

The various kinds of steel we find in everyday life are alloys of iron with nickel, manganese, tungsten, chromium, vanadium, molybdenum, and other metals. Brass usually contains 30% zinc and 70% copper. Bronze is composed of 5% tin, 15% zinc, 75% copper, and a small quantity of lead. German silver is a mixture of copper, zinc, and silver. Gun-metal is a mixture of copper and tin.

Our silver coins are alloys, containing about 90% silver and 10% copper. Our nickels are only 25% nickel; the rest is copper.

Solder

We will have to confine our home experiments to metals with low melting points, as we assume that not many home labs are equipped to melt such metals as iron, silver, copper, nickel, etc. Metals such as lead, tin, antimony and bismuth form many interesting alloys and an alcohol lamp will supply sufficient heat to melt them.

Perhaps the best known of the low-melting alloys is common solder. It is very easily made and consists of equal quantities of tin and lead.

Place the metals in a crucible and apply sufficient heat to melt them. After they are entirely molten and thoroughly mixed, pour into a mold or any metal container. That's all there is to it. You now have a genuine solder, and it can be used as such.

Wood's Metal

Wood's Metal is an unusual alloy because of its extremely low melting point. It melts at 70 degrees C., which is below the boiling point of water!

Mix together 4 grams of tin, 8 grams of lead, 3 grams of cadmium, and 16 grams of bismuth. Melt in a crucible as before.

Place a small quantity of Wood's Metal in the bottom of a large test tube half filled with water. Heat. If you observe closely, you will see the metal melt before the water boils.

Rose's Metal

Another low-melting alloy is Rose's Metal, which melts at 94 degrees. You can prepare it by melting together 10 parts of bismuth, 55 parts of lead, and 5 parts of tin.

These low-melting alloys are quite useful in such devices as electric fuses,

automatic sprinkler systems, automatic fire alarms, safety plugs for boilers, etc. For example, you can appreciate the value of the alloy in a sprinkler system in case of fire. The heat of the flames will easily melt the alloy, thereby releasing large quantities of water which, it is hoped, will extinguish the fire before serious damage occurs.

Pewter

Pewter consists of 8 parts tin and 2 parts of lead. Melt together as above.

Type Metal

Melt together 1 part of tin, 16 parts of lead, and 3 parts of antimony.

Amalgams

When metals are alloyed with mercury, an amalgam is formed. They are obtained more easily with the lighter metals.

Sodium Amalgam: Place a small drop of mercury — no larger than a pea — in a mortar. Cut a still smaller piece of clean, dry sodium into very small particles. Add to the mercury and press the two elements together with the pestle. There may be miniature explosions as the elements unite, which are harmless if you use small quantities.

Sodium amalgam is decomposed by water with the evolution of hydrogen.

Ammonium Amalgam: Add a little sodium amalgam to a warm saturated solution of ammonium chloride. The amalgam swells up and forms a porous mass which rapidly decomposes.

Of course, the ammonium radical, NH_4 , has never been isolated. The above experiment is quite interesting in that it upholds the theory that if

ammonium could be isolated it would have the properties of a metal. Mercury is only miscible with metals.

Aluminum Amalgam: Aluminum amalgam is formed by the action of sodium amalgam upon metallic aluminum.

* * *

Our discussion of alloys must neces-

sarily be limited. There are hundreds of others far too numerous to mention here. Each specialized mechanical or electronic device requires metal parts which must exhibit special properties. Most of these properties can only be obtained through the use of alloys, which are becoming more useful every day.



Chapter V

Experimenting With Solutions

1. Solutions and Solubilities

A *homogeneous* mixture of two or more substances, in which the proportions of said substances usually can be varied only to certain limits, is known as a solution. In other words, if you stir a little salt in a glass of water, it will dissolve. The salt is distributed evenly throughout the water and, in general, its properties are extended evenly to all portions of the solution. In other words, the water is salty.

Now only a limited quantity of a substance will dissolve in a solvent. When all the substance that will dissolve has been added, we have what is known as a saturated solution. But there are some substances which will overdo their dissolving capacities. Under certain conditions more than the limited quantity will dissolve, and we then have a *super-saturated* solution. Like an over-inflated balloon, the continued existence of a super-saturated solution as such is rather uncertain. As a slight strain will cause the balloon to burst, so a slight disturbance will cause the substance in a super-saturated solution to separate out.

Supersaturation makes an interesting demonstration. A super-saturated solution in a large beaker is standing on the table. From all appearances, it is a beaker of water. Then a small crystal is dropped in the solution, or it is touched with a stirring rod. Sud-

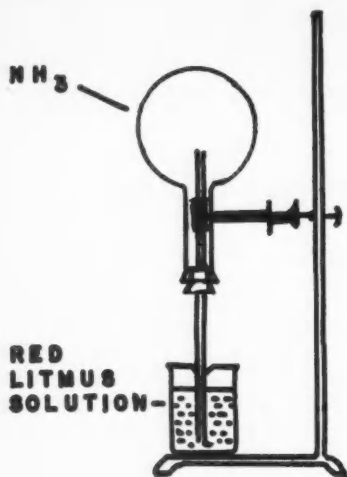
denly a large quantity of crystals separates out of the solution with amazing speed and soon the liquid turns mysteriously to a solid.

To prepare your super-saturated solution; use crystalline sodium thiosulfate, or photographer's hypo. For every 10 cc. of crystalline hypo, add only 2 or 3 drops of water. Heat gently until a clear liquid is formed. Then cover the container loosely and allow to cool. Be careful not to shake or jar the container. If crystals are formed, try again using a few additional drops of water. If desired, the solution may be cooled by immersing the container in cold water.

Gases Dissolve

Gases, as well as solids, are soluble in water. One striking example is that of ammonia gas. Under normal conditions, one volume of water will dissolve about 700 volumes of ammonia. This amazing solubility can be demonstrated in a fascinating experiment.

First the ammonia is prepared by pouring ammonium hydroxide on solid sodium or potassium hydroxide in a flask and applying gentle heat. Fill a large Florence flask with the gas by inverting it over the generator flask. The ammonia will rise into the empty flask, as it is lighter than air. Of course, it will not be necessary to warn you to keep the gas away from



➤ FOR THE ammonia fountain, the tubing should extend about two-thirds the way down beneath the surface of the liquid in the beaker. Be sure you have enough liquid in the beaker to be able to fill the flask at least one-half full.

your eyes. When you feel that the

flask is filled with ammonia, remove it, and keeping in inverted position, insert a one-hole stopper containing a length of glass tubing. Immerse the other end of tubing in a beaker of water colored with red litmus. (See diagram.) Gradually, the water will be drawn up the tube and when it reaches the top, it will spurt forth forming a spectacular fountain. The red solution will be colored blue by the alkaline reaction of the ammonium hydroxide.

If no explanation is offered, this will prove most baffling to an unscientific audience. The flask can be filled with ammonia ahead of time and securely stoppered. You will hint to the audience that it is simply an empty flask. And to further your point, you can invert the flask and remove the stopper to prove there is nothing in it. (Don't turn it right side up or the "nothing" will escape.) The water rising in the tube is contrary to all laws of gravity, and the fact that the red liquid suddenly turns blue for no apparent reason adds to the mystery.

2. Iodine Clock

Let us consider, for a moment, a crystal of common salt. It is composed of sodium ions and chloride ions held together by the powerful attraction of opposite charges — positive and negative. When this crystal is dissolved in water the ions are separated and are free to combine with other ions that may be introduced. If a solution of silver nitrate is mixed with a solution of sodium chloride, a white precipitate is formed *immediately*, thus il-

lustrating the incredible speed of the reacting ions.

Another example of the speed of chemical reactions can be shown readily in a fascinating experiment. Sometimes known as the "iodine-clock", this experiment may be familiar to you.

Two solutions are required. Solution A is made by dissolving 1 gram of potassium iodate in 500 ml. of water.

If you do not have potassium iodate, you can manufacture your own. Add 1 gram of iodine crystals to 20 or 30 ml. of warm potassium hydroxide solution. Heat if necessary to dissolve all the crystals. The reaction is: $3\text{I}_2 + 6\text{KOH} \rightarrow \text{KIO}_3 + 5\text{KI} + 3\text{H}_2\text{O}$. You will note that potassium iodide (KI) is also formed. Evaporate the solution nearly to dryness; the iodate, being less soluble, will crystallize first. Or better still, heat to dryness and dissolve the entire residue in alcohol (either grain or wood alcohol). The iodide will dissolve, leaving the iodate, which can be obtained by filtering and carefully drying.

Or, if you prefer, potassium iodate can also be prepared by oxidizing potassium iodide — KI. Mix a solution of potassium iodide with a solution of potassium permanganate, the latter in excess, and heat to boiling for a few minutes. The reaction is: $\text{KI} + 2\text{KMnO}_4 + \text{H}_2\text{O} \rightarrow \text{KIO}_3 + 2\text{KOH} + 2\text{MnO}_2$. Filter off the brown precipitate (MnO_2) and evaporate the filtrate to dryness. Alcohol will dissolve the KOH, leaving the iodate.

Now we are ready for solution B. Dissolve 0.2 grams of sodium bisulfite in 450 ml. of water. Add to this 3 ml. of molar sulfuric acid. (In case you have forgotten, a brief explanation may be in order. A molar solution contains one gram-molecular weight of the solute in 1 liter of solution. The gram-molecular weight of sulfuric acid is 98 ($\text{H}_2 = 2$; $\text{S} = 32$; $\text{O}_4 = 64$) — therefore 98 grams in 1000 ml. or approximately 1 gram in 10 ml. represents a molar solution. The specific gravity of sulfuric acid is 1.84, meaning 1.84 or approximate-

ly 2 grams occupy 1 ml.; thus 1 gram of acid in 10 ml. would be equivalent to 1 ml. of acid in 20 ml. of solution. Therefore add 1 ml. of acid to 20 ml. of water . . . and why didn't we say this in the first place?). Also add 50 ml. of starch suspension, made by dissolving 1 gram of starch in 50 ml. of hot water. Cool thoroughly before adding.

Now mix equal quantities of the two solutions. After about 20 or 30 seconds the liquid will suddenly turn blue-black without any apparent reason or cause. This appears rather baffling to those not acquainted with chemistry, which is the reason for the popularity of the experiment as a public demonstration stunt. The demonstrator, through experience and careful preparation of solutions, knows exactly when the solution will darken in color. He places the colorless liquid in view of the audience. At the exact moment he waves a "magic" wand over the vessel and the colorless solution turns black.

If you are a true scientist, you will want to know why the solution behaves as it does. We shall attempt to satisfy your curiosity.

When the solutions are mixed, iodic acid, HIO_3 , and sulfurous acid, H_2SO_3 , are formed which immediately react with each other: (1) $\text{HIO}_3 + 3\text{H}_2\text{SO}_3 \rightarrow \text{HI} + 3\text{H}_2\text{SO}_4$. As fast as the hydriodic acid (HI) is formed, it reacts with the unused iodic acid present forming free iodine: (2) $\text{HIO}_3 + 5\text{HI} \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$. The free iodine immediately reacts with any unused sulfurous acid to form hydriodic acid again: (3) $\text{I}_2 + \text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow 2\text{HI} + \text{H}_2\text{SO}_4$, and thus the cycle continues until all

the sulfurous acid is used. The free iodine then remains in solution and with the starch forms the intense blue-black color. The first reaction is slower than the last. The time required for the three reactions to reach completion accounts for the lapse of time before the change of color. The speed of the reactions can be increased by concentration or by heat.

With practice and patience, you can develop this experiment into an art. By diluting or concentrating the solutions involved you can bring about the color change at any time you wish.

If sodium bisulfite is added to the blue solution it will become colorless again. The supply of sulfurous acid is thereby replenished, and the free iodine combines with it (reaction 3 above).

This experiment vividly illustrates the remarkable regularity and intricacy that exist in the infinitesimal world of ions and molecules. Who would think that in the innocent-looking solution there is a raging inferno of reactions — combining and recombining, crashing and colliding back and forth with unimaginable speed!

3. Water Fountain

In the first experiment of this section we described an "Ammonia Fountain" in which water was drawn up a tube and spurted forth in the flask above to form a miniature fountain.

This experiment can also be performed using only water. In this instance, the air is driven out of the flask by applying heat. Atmospheric pressure then forces the water into the partly evacuated flask.

Refer to the figure accompanying Experiment 1 of this section (page 72) and set up a similar apparatus. Again it is a good idea to color the water in the beaker with litmus or other dye in order to make it more visible. In this experiment, be sure that the flask is made of Pyrex glass.

With the glass tubing immersed in the beaker of water, apply heat to the inverted flask with a Bunsen burner flame. Move the flame about in order to heat all parts of the flask evenly. The air is driven out of the flask and will bubble through the water in the beaker. Continue heating until no more bubbles are formed. Then remove the flame. The water will gradually rise in the tube and when it reaches the flask it will burst forth in a splashing fountain.

If the water does not rise all of the way into the flask, the flask must be heated for a longer period of time. Or, you may try using a shorter length of glass tubing. In most cases the water will move very slowly upward. But, be patient . . . it will eventually reach the top!



Chapter VI

Experimenting With Electro-Chemistry

► DURING RECENT YEARS, the use of electrical energy in chemical processes has become increasingly important. Many useful industrial chemicals and elements are prepared through the use of the electric current.

Conversely, chemical processes are also used to produce electrical energy. The common storage battery, dry cell

and flashlight battery are examples of this type of reaction.

As far as practical in a home lab, we shall examine the relationship of electricity to chemistry in several types of reactions. We are somewhat limited because many reactions require high voltages and high temperatures which are beyond the scope of the home chemist.

1. Source of Current

► ONE OF THE greatest accomplishments of science has been the harnessing of the electron with its resultant benefit to all mankind. In the atom, electrons are constantly spinning about the nucleus held within their orbit by the attractive force of that nucleus. By applying energy to the atom it is possible to increase the speed of these electrons and even to knock them out of their orbits into space. In a copper wire, for instance, the electrons freed from one atom will knock out electrons from the adjoining atom. The process is repeated with amazing rapidity throughout the length of the wire. This constant orderly surge of electrons constitutes a flow of *electricity*.

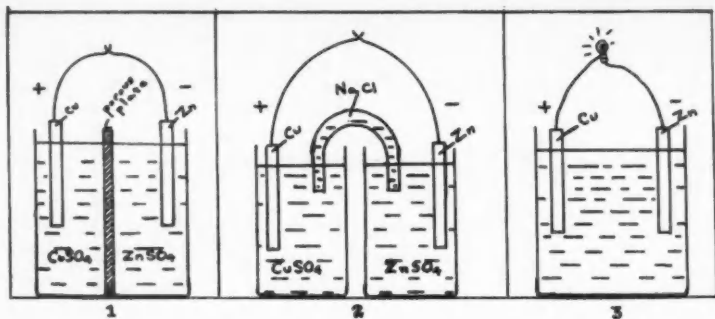
The simple mechanical energy of rubbing is sometimes sufficient to cause a flow of electrons. To demonstrate, rub a glass rod with a piece of silk, which action forces some of the

electrons in the rod to jump to the silk. The rod having lost an electron (negative charge) is now positive. The silk having gained an electron (negative charge) is now negative. If the two objects are brought together, without friction, the opposite charges will attract, the electrons consequently will move back to their original places and an electric current will flow.

Comb your hair vigorously for a few minutes; then hold the comb about $\frac{1}{4}$ inch away from a small steady stream of running water from the spigot. The stream of water will bend toward the comb, and by moving the comb you can curve the stream of water in any direction you wish.

Electro-Chemical Cells

Another method of producing electricity is by chemical reaction; this is



the method with which we are primarily concerned.

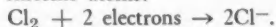
One type of cell is based on the replacement of copper by zinc: $\text{Zn} + \text{Cu}^{++} \rightarrow \text{Zn}^{++} + \text{Cu}$. However, the zinc must not be allowed to be in direct contact with the copper. To accomplish this, a porous plate is inserted in a large container so as to form two separate partitions (Figure 1). A strip of zinc is immersed in a solution of zinc sulfate on one side of the plate and a strip of copper is immersed in a solution of copper sulfate on the other side. The porous plate will prevent mechanical mixing of the solutions, but will not interfere with the passage of ions. Now if a copper wire is connected to the two electrodes, an electric current will flow through it.

If desired, two separate containers can be used for this cell as shown in Figure 2. The inverted U-tube is filled with sodium chloride solution which will permit the passage of ions.

Now just what is happening? When the metals are immersed in the solutions, they tend to form ions and consequently electrons are released: $\text{Zn} \rightarrow \text{Zn}^{++} + 2 \text{ electrons}$. However zinc is much more anxious

to make this change than is copper. Result: we have a surplus of electrons around the zinc which constitutes a difference of potential. The electrons then flow along the zinc through the wire to the copper. Here they form copper atoms from the cupric ions: $\text{Cu}^{++} + 2 \text{ electrons} \rightarrow \text{Cu}$.

Many other chemical reactions can also be used to produce an electric current. For example, sodium chloride solution can be used in both partitions of the cell. One solution is then saturated with chlorine and a stick of carbon is immersed therein. A strip of zinc is immersed in the other solution and the two connected with a wire. Here the energy is produced by an oxidation-reduction reaction. (Zinc is oxidized, chlorine reduced). The electrons, released by the zinc, pass through the wire to the carbon pole where chloride ions are formed from the chlorine atoms:



For quick demonstration purposes, it is possible to obtain an electric current by inserting electrodes in the same solution. Simply mix the copper and zinc sulfate solutions in one container and add a little sulfuric acid. Insert the metal strips (zinc and cop-

per) but do not allow them to touch [Figure 3]. We were successful in lighting a flashlight bulb with this set-up.)

Dry Cell

The dry cell utilizes solid materials in its construction instead of liquids. A zinc cup serves as the electrode. This is lined with porous paper to separate it from the solids within. The "solids within" consist of a moist mixture of manganese dioxide, ammonium chloride, some zinc chloride, and a porous inactive filler. A carbon rod is inserted in the center of the mixture which acts as the positive pole. Here the zinc is oxidized (loses electrons) to zinc ions and the ammonium ions are reduced (gain electrons) to ammonia and hydrogen: $2\text{NH}_4^+ + 2 \text{ electrons} \rightarrow 2\text{NH}_3 + \text{H}_2$. The ammonia reacts with the zinc ions to form complex zinc ammonium ions and the hydrogen reacts with the manganese dioxide as follows:



Electronics

In addition to passing through solids, electrons may also pass through a vacuum and through rarified gases with many startling results. The study of the properties of electrons in this capacity is chiefly the interest of the physicist, but we feel a few brief remarks here will be of interest.

When a metal filament inserted in

a vacuum tube is electrically heated, electrons are emitted. When another metal strip ("plate") is inserted in the tube and charged positive, it will draw all electrons to it. Sometimes a third metallic element ("grid") is inserted between the filament and plate. A positive charge on the grid will speed up the electrons and a negative charge will slow them down. Here we have the basic essentials of the electron tube and with variations we have the radio tube, amplifier tube, rectifier tube, etc.

Some metals, such as cesium and rubidium, emit electrons when subjected to light, the amount of electrons emitted depending upon the intensity of light. These electrons can be concentrated, amplified and converted into high-frequency oscillations which in turn can be transmitted through space by radio waves. Thus we have one of the basic principles of television.

When certain gases are bombarded with electrons, energy is given off as light—the basis of the familiar "neon" signs.

In addition to mechanical motion, heat and light, electrons can also produce sound. The tone of such an instrument as the Hammond Organ is created by the amplification of electrical impulses into sound waves. This remarkable instrument is capable of producing some 253,000,000 different tones!

2. Electrolysis

We have discussed the formation of an electric current as a result of chemical reaction; now we will investigate the effect an electric current has on chemical compounds.

This is not a novel idea. Sir Humphrey Davy thought of it more than one hundred years ago. His research in the field of electro-chemistry was highlighted by the isolation

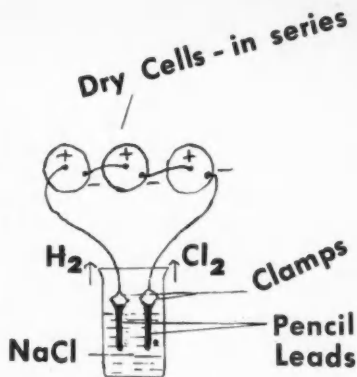
of the alkali metals. After several unsuccessful attempts to decompose aqueous potash solutions with an electric current, Davy used potash in igneous fusion. When an electric current was passed through the compound, amazing things began to happen. There was violent effervescence throughout with the formation of small globules, or in Davy's own words:

"... at the negative surface, there was no liberation of elastic fluid; but small globules having a high metallic lustre, and being precisely similar in visible characteristics to quicksilver, some of which burnt with explosion and bright flame as soon as they were formed, and others remained and were merely tarnished and finally covered by a white film which formed on their surfaces."

We can well imagine how excited and joyous Sir Humphrey Davy must have been. Here was a new powerful force — the electric current. How would it react on other substances? Could additional elements be isolated? Indeed they could, for following in rapid succession sodium, barium, strontium, calcium, magnesium and lithium were isolated by means of the electric current. And using the sodium and potassium prepared by electrolysis the elements zirconium, titanium, cerium, thorium, beryllium, boron, silicon, and aluminum were isolated.

Source of Current

But let's get back to the home lab. Of course, a direct current is required for these experiments. Three or four dry cells may be used or two 3-volt "utility" batteries. The storage battery from the family automobile is also



➤ APPARATUS set-up for experiments with electrolysis.

satisfactory. If you use dry cells, connect them in series, that is, the positive terminal of one cell to the negative of the other. For the electrodes, use small carbon rods. Pencil leads will serve very nicely in this capacity.

Aqueous Sodium Chloride

Let us briefly consider a solution of sodium chloride. We have positively charged sodium ions and negatively charged chloride ions migrating throughout the solution. In addition the water provides a small quantity of ions—positive hydrogen and negative hydroxyl. To summarize, the solution contains Na^+ , Cl^- , H^+ , and OH^- .

When the two electrodes from a source of electricity are immersed in this solution, what happens? Well, as you might expect, the positively charged ions (Na^+ , H^+), are attracted to the negative electrode and the negative ions (Cl^- , OH^-) to the positive electrode. The hydrogen ion re-

moves an electron from the negative electrode and thus becomes a hydrogen atom. The sodium ion, however, is much more reluctant in accepting electrons and will not do so unless forced to by a greater current of electricity.

Meanwhile the negative ions (Cl^- , OH^-) are moving toward the positive electrode. Here the chloride ion loses an electron and becomes a chlorine atom. The more selfish hydroxyl ion will not readily give up its electron and hence remains in solution 'status quo.'

Now we have hydrogen released at the negative and chlorine at the positive. The sodium and hydroxyl ions remaining in solution combine with each other forming a solution of sodium hydroxide.

To demonstrate the above, simply electrolyze a salt solution to which a few drops of phenolphthalein solution have been added. Almost immediately the solution will turn pink indicating the presence of sodium hydroxide. (If your salt solution turns pink upon addition of phenolphthalein before electrolysis, use potassium chloride or chemically pure sodium chloride. This alkaline reaction is probably due to the presence of magnesium carbonate added to table salt to keep it "pouring when it rains.>"). As electrolysis is continued you will be able to detect the odor of chlorine. Some of the chlorine dissolves in the solution and reacts with the sodium hydroxide forming sodium hypochlorite:



This mixture of salt and sodium hypochlorite is known as *Javelle Water*,

sold commercially as a bleach for the home laundry. It is also useful as an antiseptic, sodium hypochlorite being an efficient bactericidal agent.

Thus with salt solution as our starting point, we obtain hydrogen, chlorine, sodium hydroxide, sodium hypochlorite, and Javelle Water.

Electrolysis of Water

There are two general methods of acquiring knowledge: (1) by studying the opinions and findings of others; (2) by actual experience and personal observation. The latter method is particularly applicable to the study of science.

Let us consider the composition of water. We have read in chemistry textbooks that water consists of two parts hydrogen and one part oxygen. This is simply accepting the findings of others; let us actually *prove* this statement to our own satisfaction.

The best way to determine the composition of a substance is to decompose it into its component parts and then identify each one. With water, we can accomplish this by electrolysis.

As water does not conduct the electric current, a small amount of sulfuric acid must be added to make a conducting solution. Set up an apparatus similar to the one shown. A shallow pan or trough is filled partly with the solution. Two test tubes or narrow bottles are also filled and inverted in the solution in the trough. Finally the electrodes from a source of direct current are inserted — one in each tube. Four dry cells should provide sufficient current for this demonstration. The electrodes should be of platinum, but if your supply of

this metal is exhausted, strips of carbon (pencil leads) will suffice.

As electrolysis is begun, you will notice bubbles of gas arising from the electrodes which will gradually displace the water in the tubes. You will notice also that twice as much gas is obtained from the negative electrode as from the positive. If the textbooks are correct, this must be hydrogen.

Finally, when all water is displaced, stopper the tubes quickly and then remove from the solution. Now we should have hydrogen in the negative tube and oxygen in the positive. Invert the tube of hydrogen, remove the stopper, and hold over an open flame. A sharp explosion will confirm the identity of hydrogen. Remove the stopper from the oxygen tube and quickly insert a glowing splinter. The splinter will burst into flame thus proving the presence of oxygen.

Therefore in reality we have proved that water consists of hydrogen and oxygen in the ratio of 2 to 1. We have learned something through personal observation and findings. Such is the purpose of experimenting.

Metals by Electrolysis

By passing an electric current through a solution of silver nitrate, metallic silver can be obtained. Allow the carbon electrodes to dip in the solution. You can actually see crystals of silver growing on the negative rod.

Copper may be obtained in a similar way from copper sulfate solution.

In fact, most of the less active metals can be obtained in this manner: lead, tin, mercury, gold, etc.

The metals will always be liberated at the negative pole. Can you determine by experimentation alone (without reference to any text books) what is liberated at the positive pole?

The more active metals cannot be liberated from their aqueous solutions by electrolysis. As we explained, the electrolysis of sodium chloride solution will not produce sodium. Here it is necessary to electrolyze the sodium chloride in a molten state to obtain the metal. This requires an extremely high temperature and a strong current of electricity and is not recommended for the home lab.

Commercially, both sodium and chlorine are produced by the electrolysis of molten salt. Potassium is obtained by the electrolysis of molten potassium hydroxide.

Calcium, barium and strontium can also be obtained by electrolyzing the fused chlorides.

Aluminum is obtained by the electrolysis of a solution of aluminum oxide in fused cryolite.

Magnesium can be obtained by electrolyzing a fused mixture of magnesium, sodium, and potassium chlorides; or by electrolysis of magnesium oxide dissolved in fused magnesium fluoride.

Thus we see the important role electricity plays in the production of many vital metals.

3. Electroplating

Our study of electrolysis would not be complete without a consideration of electroplating. Chemists have

brought the beauty and durability of rare and expensive metals within the reach of everyone by this simple pro-

cess of coating an inexpensive metal with a thin layer of a more valuable one.

For electroplating, only a small direct current is required. Two or three dry cells should be sufficient. The object to be plated is made the cathode, and a strip of the pure metal to be deposited is made the anode. The whole is immersed in a solution of a salt of the metal to be deposited.

The metal to be plated must be thoroughly clean and free of grease. Scrape any rust or corrosion with a wire brush or steel wool. Then immerse in a boiling solution of washing soda. Finally, place in a "pickling bath" of dilute sulfuric acid.

Copper Plating

The size of the object to be plated will determine the quantity of the electrolytic bath required. The entire object should be immersed in the solution.

For every 25 cc. of water, use approximately one gram of copper sulfate. Better results are obtained if a small quantity of gelatin is added to the solution. Attach a strip of pure copper to the positive wire of your cell and the object to be plated to the negative wire. Immerse both wires in the copper sulfate solution, but do not allow them to touch.

The thickness of the plate will depend upon the strength of the current and length of time employed. You must use your own judgment to determine when a proper plating is attained.

Nickel Plating

Proceed as above, using for the electrolyte a solution of nickel ammonium sulfate—about one gram to 25 cc. of water. Add to this solution

a small quantity of ammonium chloride, boric acid, and gelatin. The anode in this case will be a pure strip of nickel. Try nickel plating a copper penny.

Cobalt Plating

Although not practiced widely commercially, it is possible to plate with cobalt as well as nickel. The electrolytic solution is the same as that for nickel with cobalt chloride used in place of nickel ammonium sulfate. And, of course, cobalt metal must be the anode.

Zinc Plating

As you probably know, zinc is used to form the protective covering on galvanized iron. The zinc can be applied by spraying the molten metal on the iron, by dipping the iron in the melted zinc, or by electroplating. For the latter method, a solution of zinc sulfate is used.

Chromium Plating

Because of its brilliant lasting luster, hardness, and resistance to corrosion, chromium is perhaps the most popular of electro-plated metals.

Articles to be plated with chromium are usually nickel plated first. The electrolyte is a solution of chromic acid (chromium trioxide), and the anode is pure chromium. Chromic acid is a powerful oxidizing agent and must be handled carefully.

Silver Plating

In plating with silver, the metal is liable to be deposited as a large spongy mass or a loose powder. In order to prevent this, potassium cyanide is added to the plating bath to cause the silver to plate out more slowly. With silver nitrate the complex silver-cyanide ion, $\text{Ag}(\text{CN})_2$, is formed. This

ion is only slightly ionized thereby reducing the concentration of silver ions in the solution; hence the metal is deposited more slowly and evenly.

To a solution of silver nitrate, add about one-half as much potassium cyanide and a small quantity of gelatin or glue. Now we must pause for a word of caution. *Remember—the poisonous qualities of potassium cyanide have not been exaggerated! You must be careful!* Wash all utensils immediately after using. Do not allow the liquid to spill on your skin. Do not allow the cyanide to come into contact with any acid.

Proceed to electroplate as with previous metals using a small piece of pure silver as the anode.

Gold Plating

If you can afford it you can also gold plate by using a solution of gold potassium cyanide (*poisonous!*), or a solution of gold trichloride (chloroauric acid), $\text{AuCl}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$.

* * *

There are many "tricks of the trade" in electroplating. Type of current, strength of current, type of bath, composition of article to be plated, concentration of bath, etc. all play an important part in the quality of the finished product. By working carefully, taking your time, and trial experimenting, you will soon be in a position to do a good job of plating on many household articles.

4. Electrochemical Series

► ONE OF THE finest examples of the systematic relationship of the chemical elements to each other is shown in the Electrochemical Series of metals. This Series is merely a list of the metallic elements arranged in the order of their decreasing chemical activity. Suppose we take the familiar metals and list them accordingly:

Potassium
Sodium
Barium
Strontium
Calcium
Magnesium
Aluminum
Manganese
Zinc
Chromium
Cadmium
Iron
Cobalt

Nickel
Tin
Lead
HYDROGEN
Copper
Arsenic
Bismuth
Antimony
Mercury
Silver
Platinum
Gold

You will note that the metals at the top of the list are exceedingly active, those in the middle are moderately active and those near the bottom are relatively inactive. Also, note that we have included hydrogen in this list. Here it acts as a dividing line. All of the metals listed above hydrogen will liberate it from acids or water; those listed beneath it will

not. For example, the metals down to calcium will liberate hydrogen from cold water. The metals from magnesium through iron will liberate hydrogen from boiling water or steam. The metals from cobalt through lead will only liberate hydrogen from acids.

To demonstrate the decreasing activity, prepare a dilute solution of hydrochloric acid and pour equal quantities into five test tubes. Now in the first tube drop a piece of magnesium; zinc in the second; iron in the third; tin in the fourth; and copper in the fifth. Note that the magnesium dissolves rapidly, the zinc fairly rapidly, the iron moderately, the tin slower and the copper is not affected.

Another factor to consider in the Electrochemical Series is the *displacement* of one metal by another. Any metal in the Series will displace from solution any other metal which comes below it in the list. Thus, a piece of iron will displace copper in a solution of copper sulfate and will itself go into solution as iron sulfate. Copper, in turn, will displace silver from a solution of silver nitrate. Silver will displace gold from solutions of gold salts.

Prepare a solution of copper sulfate and drop a piece of steel wool into it. In a few minutes the wool will be covered with a deposit of metallic copper. You can make a "copper" nickel by dropping a nickel coin in a solution of copper sulfate. Here the action is much slower, as the coin is an alloy containing only a small percentage of nickel.

Drop a piece of clean magnesium in a solution of nickel sulfate. Let stand for a while and then examine the magnesium for the presence of nickel.

The displacement of lead can be demonstrated with the familiar "lead tree" experiment. Dissolve 5 grams of lead acetate in 50 cc. of water and add a few drops of acetic acid. Pour into a beaker and suspend a strip of zinc in the solution. After a short time the zinc will be covered with brilliant crystalline spangles of metallic lead.

Or, perhaps you prefer a "silver tree." Prepare a solution of silver nitrate in a beaker. Place a globule of mercury in a small linen bag and immerse it in the solution. After standing a few hours, crystals of silver will be displaced and will cling to the bag.

Metallic tin can be isolated by displacement. Prepare a strong solution of stannous chloride. As before, suspend a zinc rod or strip in the solution. Allow to stand for several days when a mossy deposit will form on the zinc. Remove from the solution, scrape off the deposit and dry by squeezing between sheets of filter paper. The deposit consists of minute crystals of tin.

You can use the displacement of mercury by copper to make a "silver" penny. Drop a clean copper penny in a solution of mercuric chloride. After an hour or so remove the coin. To bring out a silvery luster rub the coin briskly with a soft cloth.

You can obtain metallic silver in the same way. This time place the coin in a solution of silver nitrate. (The deposited silver will not cling to the coin as well as the mercury; hence mercury makes the better "silver" penny). Collect the little plates of pure silver after allowing the solution to stand for a few days.

Maybe you have been wondering why this list of metals is known as

the *electro*-chemical series, or as the *electro*-motive series. The reason is that the *voltages* shown on the voltmeter decrease down the list when the metals are used as a negative electrode in a voltaic cell. In all cases, a carbon rod is used as the positive electrode. In other words, the metals are listed in the order of the ease with which they lose electrons.

If you have access to a sensitive voltmeter you may like to try this. Use a very dilute solution of sulfuric acid as the electrolyte and place it in a large wide-mouth jar or beaker. Insert a carbon rod in one portion of the liquid and a metal near the top, such as magnesium or aluminum, in the solution opposite the carbon. Do not allow the two materials to touch each other. Now connect the two electrodes together by means of the voltmeter. Remember, a voltmeter is always connected in parallel with an electric circuit which means that the positive lead should be connected to

the positive electrode (the carbon) and the negative lead to the negative electrode (the magnesium or aluminum). Note carefully how far the needle is deflected. Now repeat the procedure using a metal further down the list such as iron or lead, instead of the magnesium or aluminum. Observe in this case the needle of the voltmeter is not deflected as far as before which means there is a decreased voltage, hence a decreased current, hence a decreased flow of electrons.

Finally, the electrochemical series tells us how easily the various metals can be obtained. The metals at the top are never found free in nature and hence are isolated only with difficulty. The metals down to cadmium are not reduced by hydrogen. The metals from iron through antimony are isolated with more ease and are readily reduced by hydrogen. The metals below antimony are often found free in nature and are very easily isolated.



Chapter VII

Experimenting With the Blowpipe

➤ THE LOWLY blowpipe has been sadly neglected in the modern laboratory, although it was once a popular instrument. However, even today it can be quite useful for home laboratory work where more complex equipment is not usually available. You may be surprised to know how much

can be accomplished through the use of the blowpipe. It does have two disadvantages in that only very small quantities of material can be worked and that the energy to operate the instrument must be supplied by the user.

1. Procedure

If you have plenty of hot air, you will be a good blowpipe operator. The formula is simply blow, blow, and blow. The best way to do this is to keep the cheeks fully inflated. Try to inhale through your nose and exhale through your mouth. This will enable you to keep a steady stream of air on the flame which is necessary for max-

imum efficiency. If you blow hard and hold the nozzle of the pipe at the base of the flame you will obtain a blue oxidizing flame. If the pipe is held slightly away from the flame, with more gently blowing, a yellow reducing flame will be obtained. We feel that an alcohol lamp flame is the most convenient for these experiments.

2. Metallurgy

It is best to perform these operations on a charcoal block. Scrape out a small cavity in the block. Place the substance to be heated in the cavity and direct the flame upon it. Do not blow so hard that you sweep the material out of the hole. We also suggest that you hold the block with tongs as a blowpipe flame is mighty hot on the fingers!

Many metals can be prepared from their compounds through the use of a blowpipe. We'll start with an easy one: lead. Place a small quantity of yellow lead oxide in the hole in the charcoal block and heat with the re-

ducing blowpipe flame. You will notice the globules of lead which form very quickly.

You can obtain silver by heating silver nitrate. Heat gently at first to drive off the water of crystallization, then apply strong heat. Examine the residue for shiny pinpoint-size globules of pure silver.

Particles of copper can be obtained by heating cupric oxide, although greater heat is required.

If you feel ambitious, you can attempt the reduction of iron oxide. The small particles of metallic iron can be separated with a magnet.

Cobalt metal can be obtained by mixing anhydrous sodium carbonate with cobalt nitrate. Heat the mixture gently at first until all water is driven off, then more strongly. As with iron,

the particles of cobalt can be separated with a magnet. Nickel can be obtained in the same way.

Bismuth can be prepared by heating the nitrate.

3. Oxidation and Reduction

The preparation of the metals as outlined above is a good example of the *reduction* process through the use of the blowpipe and the charcoal. Here the charcoal enters the reducing process by combining with the oxygen in the oxide, leaving the free metal.

You can also perform an *oxidation* reaction. Place a piece of lead metal in a porcelain crucible lid and heat it gently in the oxidizing flame. It will melt almost immediately and soon will be covered with a yellow crust of lead oxide.

4. Analysis

The blowpipe can also be used for simple qualitative analysis. The unknown powder is ground with sodium carbonate in a mortar. The mixture is transferred to the hole in the charcoal block and heated with the reducing blowpipe flame. Always heat gently at first, gradually increasing until a good hot flame is produced. The residue is then examined very carefully. A few common compounds can be identified as follows:

Aluminum salts — form a white mass, very lustrous when hot. Allow to cool and moisten with a few drops of cobalt nitrate solution. Upon reheating, a blue mass is obtained.

Ammonium salts — The odor of ammonia can be detected.

Antimony salts — The metal itself is obtained as a brittle white bead. The cavity in the charcoal is lined with a bluish-white crust.

Arsenic salts — A garlic-like odor is obtained. (Careful: poisonous!)

Bismuth salts — As with antimony,

the metal itself is formed. This time the charcoal cavity is lined with a yellow crust.

Cadmium salts — A reddish-brown lining is formed on the charcoal.

Chromium salts — Add a little potassium nitrate and heat. A yellow substance is obtained.

Gold salts — The metal is obtained — a yellow bead.

Magnesium salts — When treated with cobalt nitrate solution as with aluminum, above, a pink mass is obtained after reheating.

Manganese salts — Heat with potassium nitrate. This time a green mass is obtained.

Mercury salts — The charcoal is lined with either a bright yellow or scarlet coating.

Tin salts — The metal is obtained — malleable white beads, easily melted.

Zinc salts — Apply the cobalt nitrate test (see "Aluminum"). A green mass is obtained.

5. High Temperatures

As you may have deduced by now, a very hot flame can be produced by the blowpipe. Just how hot can be shown by melting some common metals. For this purpose we used a porcelain crucible lid. The metal is placed in the lid and the flame directed upon it. It is important that a

steady flame is produced. The secret is to keep blowing without breathing . . . if you can accomplish this! We have succeeded in melting zinc, antimony, magnesium, aluminum, silver, and copper by this method. How many can you melt?

Happy blowing!



Chapter VIII

Experimenting With Non-Metallic Elements

1. Boron

➤ EVERYONE is familiar with borax as a cleansing agent and the properties of boric acid as an eyewash are well known. We all have, no doubt, at some time washed our hands with borax and our eyes with boric acid. But despite the popularity of these compounds of boron, the element itself is a rarity to the average person.

Boron has had very few uses in the elemental state and it is difficult to prepare with any degree of purity. Consequently, its production has been limited and its price high.

Recently, much interest has been aroused in boron and no doubt we will hear more about it as time goes on. The new "exotic" fuels designed for rockets, supersonic planes, and guided missiles are made chiefly from the compounds of boron and lithium. These compounds are quite new and very expensive at present. However, the future may bring cheaper methods of production and make their use practical for commercial airplanes and even as additives for automotive fuels.

Although details on most of these new fuels are not available because of security purposes, one method uses the compound known as *diborane* which is capable of producing 32,000 BTU per lb. It is prepared by reacting lithium hydride with boron trifluoride.

In combination with phosphorus, boron forms a group of entirely new plastics which present a possibility of future development. As boron stops neutrons from a nuclear reactor, it has been suggested that some of the new boron plastics could be used as a shield in atomic-powered airplanes.

Boron has also been utilized in the organic field. Methyl borate, for example, is used as a fungicide for citrus fruit. A group of organo-boron compounds containing 17% or more of boron known collectively as "boroximes" have been developed. These compounds are so new that few uses have been found for them as yet.

Other possibilities include several new metal alloys and new developments in glass fibers. Certainly the chemistry of boron and its many interesting compounds is still incompletely explored and much additional work needs to be done.

It was in 1808 — when Beethoven was composing his greatest music and Napoleon was rising to his greatest power — that boron first appeared as a new element. Its isolation was accomplished by Thenard and Gay-Lussac in France and Davy in England. They decomposed boric acid by heating it with potassium.

This procedure is both dangerous and costly and boron is usually pre-

pared now by reducing the oxide with magnesium: $B_2O_3 + 3Mg \rightarrow 3MgO + 2B$. This method can most easily be employed in the home laboratory.

First it is necessary to prepare the boron trioxide. Place about 5 grams of boric acid in an evaporating dish and heat thoroughly for five minutes in order to drive off the water. Actually, three reactions occur during this heating. The acid first loses a molecule of water to form metaboric acid: $H_3BO_3 \rightarrow HBO_2 + H_2O$. Upon further heating the tetraboric acid (parent acid of borax) is formed: $4HBO_2 \rightarrow H_2B_4O_7 + H_2O$. And finally, the oxide: $H_2B_4O_7 \rightarrow 2B_2O_3 + H_2O$. We are, of course, concerned with the oxide, which is a brittle, semi-transparent, glass-like solid.

Break off a few chunks, and grind in a mortar to as much of a powder as possible. Now take about $\frac{1}{2}$ to 1 gram of oxide and mix it thoroughly with an equal amount — by weight — of magnesium powder. Place the mixture in a crucible, cover it, and heat to redness. It is advisable to continue heating at this temperature for at least fifteen minutes. Then allow the crucible to cool thoroughly; remove the cover, and examine the contents.

The grayish-black mass contains free boron, magnesium oxide, mag-

nesium and a little magnesium boride. Boron is insoluble in hydrochloric acid; therefore it is possible to dissolve the other products in the acid, leaving the boron as a residue. Scrape the contents from the crucible into a beaker and add dilute hydrochloric acid. Keep adding acid and water from time to time until you are pretty sure that all soluble substances have dissolved. Then filter and dry the residue; wash with water and dry again. The product is impure boron. It usually is obtained as an amorphous brown powder.

Boron can also be obtained in the crystalline state as grayish-black, hard, lustrous crystals. It is possible to crystallize boron from molten aluminum, although the product contains aluminum boride. You can attempt this crystallization by melting a few pieces of aluminum in a crucible. Sprinkle the amorphous boron in the molten liquid and pour the contents into a large container of water. The aluminum is then dissolved in hydrochloric acid, leaving the free boron.

It is also possible to obtain boron by heating borax with red phosphorus, the reaction depending upon the strong affinity of phosphorus to oxygen. In all cases the boron is impure. Recently, boron has been obtained in a high state of purity by electrolysis of boron chloride using high-potential alternating current arcs.

2. Iodine

► IODINE, the most beautiful and most gentle member of the halogen family, first saw the light of day in 1811 when it was isolated by Bernard Courtois from the mother liquor obtained from

algae. Upon adding an excess of sulfuric acid to a concentrated portion of the liquor which he prepared by extracting the ashes of marine plants with water, Courtois was no doubt

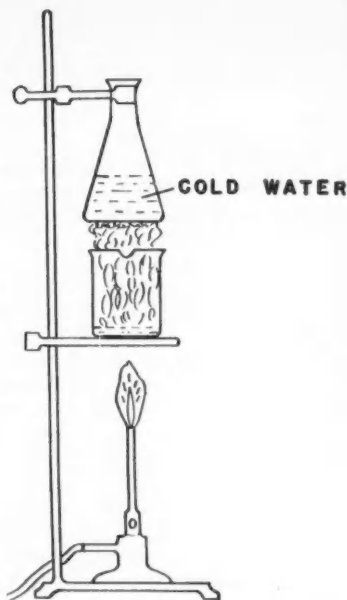
greatly surprised to see lovely clouds of deep violet vapor arising from the liquid. He found that this vapor would condense to form dark lustrous crystals, and that these crystals would combine directly with certain metals, with phosphorus and with hydrogen. Later investigation by Gay-Lussac proved the substance to be a new element and it was christened *iodine*, from the Greek word meaning "like a violet."

To prepare iodine, mix together 2 grams potassium iodide and 3 grams manganese dioxide. Transfer the mixture to a small beaker and add 10 cc. of dilute sulfuric acid. Gentle heat will produce clouds of violet iodine vapor. Place a flask of cold water over the beaker, or cover the beaker partially with an evaporating dish. Crystals of iodine will form on the bottom of the flask or dish. The iodine passes from the gaseous state directly to the solid state. This process is known as *sublimation*. Scrape the crystals off and dry them on blotting or filter paper.

To the average person iodine is known only in the form of the tincture, used as an antiseptic, which is a solution of iodine in alcohol. The medicine-cabinet variety usually contains 2% iodine. Although some people prefer the bright red of Mercurchrome to the brown of iodine, the latter's efficiency as an antiseptic cannot be denied.

Iodine will also dissolve in carbon tetrachloride or disulfide, forming a violet solution.

Another antiseptic compound of iodine is *iodoform*, CHI_3 , a yellow powder with a characteristic "antiseptic" odor. Dissolve iodine crystals



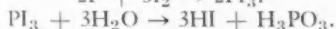
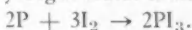
➤ SUBLIMATION of iodine.

in potassium iodide solution until the liquid is dark brown in color. Add 5 cc. of this solution to an equal amount of alcohol. Now add sodium hydroxide solution in small proportions until the brown color disappears. Upon heating a few minutes and then cooling, a yellow precipitate of iodoform will separate out.

Another and perhaps better method of preparing iodoform is by dissolving 1 gram of potassium iodide in 20 cc. of water and adding 1 cc. of acetone. To this mixture add a dilute solution of sodium hypochlorite (you can use "Chlorox" from the grocery store). The yellow precipitate of iodoform is immediately formed.

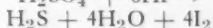
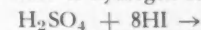
The direct combination of iodine and phosphorus forms an exciting demonstration as these two elements celebrate their union with a spontaneous display of fire. In a large evaporating dish, carefully place a *very small* piece of white phosphorus. Drop on the phosphorus a few small crystals of iodine. Keep your face a safe distance away. The mixture will suddenly burst into a brilliant flame, evolving large clouds of smoke. The result of this elaborate performance is a red compound, phosphorus triiodide, PI_3 .

With red phosphorous, the action is much milder. If water be added to the mixture of red phosphorous and iodine, hydrogen iodide is formed:



Speaking of hydrogen iodide, one would suppose it could be formed by the addition of sulfuric acid to an iodide (similar to hydrogen chloride). But such is not the case. Add a little sulfuric acid to a few crystals of potas-

sium iodide in a dry test tube. You will notice the violet vapor of iodine and if you smell at the mouth of the tube you will no doubt recognize the delightful aroma of hydrogen sulfide. Now how did hydrogen sulfide get into the picture? Well, it appears that hydrogen iodide was temporarily formed, but it, being much less stable than hydrogen chloride, is therefore a more active reducing agent. And the nearest thing around for it to reduce is the sulfuric acid, and it promptly reduces same to hydrogen sulfide:



If you add a solution of sodium thiosulfate to a solution of iodine in potassium iodide, the brown color will entirely disappear. Hence this thiosulfate is an effective agent for removing iodine stains. You may use it to remove any brown stains you have acquired on your hands. Of course, if you have been a careful worker, there will be no stains to remove. . . .

3. Sulfur

► THROUGH its evil-smelling compounds, sulfur has gained a rather bad reputation. Although many sulfur compounds do yield an offensive odor, the element itself is odorless and tasteless.

Despite the bad smells, sulfur is an extremely useful substance. One of its compounds, sulfuric acid, is the most useful chemical substance ever manufactured. About 10,000,000 tons of it are consumed each year in the United States alone. Another important use of sulfur is in the vulcaniza-

tion of rubber. It is also used in fungicides, gunpowder, fumigants, and in the manufacture of hundreds of important compounds.

Sulfur has been known since the dawn of history. It was used as a fumigant and in medicine as early as 1000 B.C. It is the "brimstone" of the Bible.

Allotropic Forms

Rhombic Crystals. Sulfur exists in two allotropic crystalline forms, the most stable of which is the rhombic.

Dissolve about 0.5 gram of sulfur in 4 cc. of carbon disulfide. If necessary, filter the solution. Pour the clear filtrate in a watch glass and allow to evaporate spontaneously. Do not heat. Examine carefully the crystals that remain. Note the formation — like two pyramids base to base.

Monoclinic Crystals. Heat gently a small amount of sulfur in a dry test tube. Heat until the sulfur just melts to a thin, light amber colored fluid. Be careful not to overheat. Pour the liquid into a dry filter paper in a funnel. As soon as a portion of the liquid begins to solidify, quickly pour off the excess liquid. Open the filter paper and examine the crystals with a magnifying glass. Note this time they are long, transparent and rectangular shaped.

Amorphous (Plastic) Sulfur. Heat again about one gram of sulfur in a dry test tube. It will melt to the amber-colored fluid. Continue heating. The liquid will turn dark orange and finally into a black mass. Continue to heat until the mass is again fluid and just begins to boil. Then pour quickly into a beaker of cold water. Do this carefully, as the vapor may ignite. Examine the mass in the beaker. You will note that it is plastic and elastic, similar to rubber. However, this condition is not permanent. Upon standing it becomes brittle and returns to the rhombic form. The strange part of it is that in this condition, sulfur is not soluble in carbon disulfide. Also, a minute trace of sulfuric acid must be present in the sulfur in order for it to be plastic. Absolutely pure sulfur does not form the plastic allotropy.

Colloidal Sulfur (Milk of Sulfur). Colloidal sulfur consists of small

rhombic crystals. It is formed readily by adding a few drops of hydrochloric acid to a solution of sodium thiosulfate. When the acid is first added, nothing appears to happen. Then, after a few seconds, a white color is suddenly formed which rapidly develops into a yellow precipitate of colloidal sulfur.

Sulfides

Sulfur combines with most of the metals and many of the non-metals to form sulfides. Here are a few of them:

Iron Sulfide. Heat equal portions of powdered sulfur and iron filings in a metal crucible or lid. Heat until the sulfur ceases to burn. The remaining mass is ferrous sulfide.

Hydrogen Sulfide. Break up a few lumps of the ferrous sulfide just prepared. Place in a test tube and add dilute hydrochloric acid. You will soon recognize the rotten-egg odor of hydrogen sulfide.

Zinc Sulfide. The formation of zinc sulfide is accompanied by a pyrotechnical display, which has been described previously (page 30).

Mercuric Sulfide. It is not even necessary to apply heat to obtain mercuric sulfide. Simply grind together a small globule of mercury with a little sulfur in a mortar. A black amorphous powder is obtained. However, if the two elements are heated together, the red variety of mercuric sulfide (vermilion) is obtained.

Oxides

As you probably have observed by now, sulfur burns in air with a blue flame forming *sulfur dioxide*. SO_2 . And as you have probably noticed by now, the latter has a pungent, ir-

ritating odor. Sulfur dioxide is a very interesting and useful compound. (See page 12).

When sulfur dioxide is interacted with oxygen, by means of a suitable catalyst, *sulfur trioxide*, SO_3 , is obtained. It is a white solid which dissolves in water to form sulfuric acid.

Other oxides of sulfur have been isolated. If you are interested, they are the *monoxide*, SO , a gas formed by the action of an electric discharge on sulfur dioxide and sulfur vapor at low pressure; the *sesquioxide*, S_2O_3 , a blue-green solid; and the *heptoxide*, S_2O_7 , a thick liquid.



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